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FEASIBILITY STUDY OF THE DISPOSAL OF POLYETHYLENE PLASTIC WASTE

Kurt Gutfreund

IIT Research Institute

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1971

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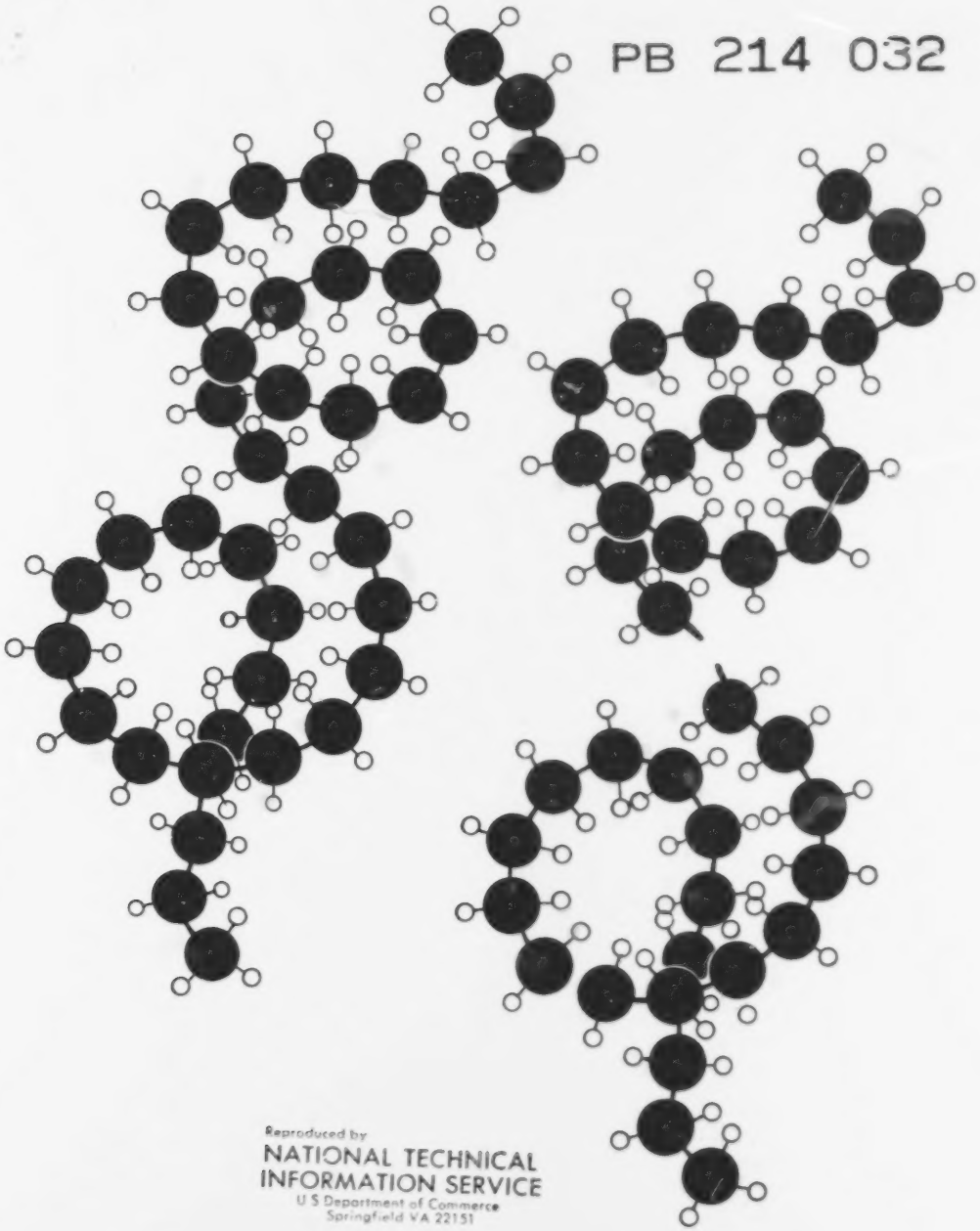

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FEASIBILITY STUDY OF

The Disposal of Polyethylene Plastic Waste

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FOREWORD

THE PLASTICS INDUSTRY has created an impressive record in developing many kinds of plastics for industrial and domestic use. The versatility of shape, size, color, thickness, strength, and density, as well as resistance to attack by other substances, has catapulted plastic containers into wide use for beverages, foods, cosmetics, and toiletries. In addition to being formed into containers *per se*, plastics appear as coatings and laminants—in combination with metal, glass, and paper—thereby permeating the entire packaging field. As a result, today's packaging waste reflects not only a rapid growth of plastics but also a decline in wood and textiles.

Packaging wastes thus constitute a significant and growing fraction of the total solid waste load. Of the 350 million tons of residential, commercial, and industrial solid wastes generated in 1966, for example, 13 percent was discarded packaging materials. In a typical year, Americans will throw away 48 billion cans, 26 billion bottles, 4 million tons of plastic, and 30 million tons of paper. Per capita generation of packaging wastes in rising steeply. In 1958, 505 pounds of packaging materials were discarded on an annual per capita basis; this figure had risen to 525 pounds by 1966. If present projections are accurate, it will reach 661 pounds per capita by 1976, unless the means are found to modify this trend.

A national research and development program was initiated by Congress with passage of the 1965 Solid Waste Disposal Act in an effort to deal more effectively with the Nation's volumes of solid wastes. As part of this effort, IIT Research Institute was asked—through the contract mechanism—to explore several approaches to facilitate the disposal of polyethylene wastes. Special emphasis was to be placed upon methods that would (1) enhance the brittleness of this polymer, (2) reduce its resistance to combustion, and (3) promote its biodegradability. Throughout the term of the contract, the Federal solid waste management program was represented by E. P. Floyd as Project Officer.

We trust that the resultant volume, which reports IITRI's study of the plastic waste disposal problem, the degradation of hydrocarbon polymers, and the results of experimental investigations, will provide some much needed basic information. Perhaps this report will also stimulate and encourage other workers to continue the search for imaginative and varied solutions to match the array of disposal problems posed by the versatile plastics.

—RICHARD D. VAUGHAN
Deputy Assistant Administrator
for Solid Waste Management

PREFACE

This is Report No. IITRI-C6120-11 (Final Report) on IITRI Project No. C6120 entitled, "Feasibility Study of the Disposal of Polyethylene Plastic Waste." The work reported herein was conducted for the Public Health Service, Solid Wastes Program under Contract No. PS-86-67-274 during the period from June 29, 1967 through September 28, 1968.*

Kurt Gutfreund, Senior Chemist, Polymer Research, was the Project Leader. The assistance of J. O'Neill in interpreting infrared data, of I. Lesevicius, who performed DTA measurements, of C. Hagen and P. Barbera, who conducted biodegradation studies on polyethylene, and of R. Glass, V. Adamaitis, and T. Meyers, who assisted in various experimental measures, is gratefully acknowledged. Thanks are also due to E. P. Floyd, the Project Officer of this project for helpful suggestions, and to T.H. Meltzer and G.A. Zerlaut, who provided technical and administrative guidance for this work.

—K. GUTFREUND, *Project Leader*
Polymer Research Chemistry

*The Solid Wastes Program is now the Office of Solid Waste Management Programs of the U.S. Environmental Protection Agency.

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FEASIBILITY STUDY OF

The Disposal of Polyethylene Plastic Waste

THE TIME IN WHICH WE LIVE has often been characterized as an age of plastics. This is in recognition of the ever-increasing amounts of polymeric materials that are fabricated and employed to fill the numerous needs of our civilization. Many kinds of polymers are manufactured today. The major plastic types in tonnage production are polyethylene, polystyrene, and polyvinyl chloride. The overall production data for these materials and their applications in products used by consumers are increasing (Table 1).

Although the home market for plastic products is small in proportion to the total volume of synthetics manufactured in this country, this market deserves consideration in municipal waste disposal problems, because consumer goods are increasingly reaching their final destination in public disposal sites.

The production of polyolefins, which include polyethylene as a major constituent, has steadily increased during the past decade and is expected to reach a volume of 6 billion lb by 1969. Polyethylene is therefore entering communal and industrial wastes in substantial amounts. About 40 percent of polyethylene waste derived from commercial sources is burned in incinerators. Disposing of polyethylene by burning it in combustion units is not entirely satisfactory, because these units are primarily designed for cellulosic materials (paper and wood) and the low-calorific constituents of municipal refuse. In general, oxygen and heat suffice to dispose completely of cellulosic derivatives by proper incineration. Polyethylene is a material that is chemically different from cellulose, and its high molecular weight and its hydrocarbon nature prevent the efficient combustion of this plastic in conventional incinerators.

Disposal of communal and industrial wastes in landfills has been attempted in this country with some success. However, this approach is restricted by economic considerations relating to the availability of landsites near metropolitan centers. The practice of burying decomposable waste (garbage, cellulosic refuse, and metals) has an advantage in that the disposal site can be reused after the materials completely decompose or corrode. However, synthetic plastics, with very few exceptions, do not undergo significant decomposition when deposited in landfills. These materials survive intact for many years, and thus delay reuse of the site. There are no known microorganisms that attack polyolefins at a rate sufficiently rapid to promote effective disposal.

It is apparent from the foregoing considerations that an efficient, safe, and economical method for the disposal of polyethylene waste is needed. A feasibility study directed toward these objectives and

TABLE 1

USE AND PRODUCTION FIGURES FOR SELECTED PLASTICS*

Plastic	Home market application	Overall U.S. production (million lb) Year 1966	1967
Polyethylene	Packaging (baking goods, produce, meat, garments)	3,448	3,632
Polystyrene and copolymers	Packing material (food containers), housewares, combs, and brushes	2,417	2,400
Polyvinyl chloride and copolymers	Clothing (outerwear, baby pants), footwear, home furnishings (upholstery, shower curtains), and garden hose	2,126	2,127

*From the plastic industry in 1967. *Modern Plastics* 45 (5): 84, 1968.

designed to determine the applicability of selected approaches to the problem of polyethylene disposal has been conducted at IIT Research Institute. Particular attention was given to chemical methods of modifying the polyolefin and the effects of the treatments on the mechanical, thermal, and biological properties of the polymer. The background and various aspects of this work are discussed in this report.

GENERAL CONSIDERATIONS OF WASTE DISPOSAL PROBLEMS

The steady population growth, changing technology, expanding economy, and higher living standards are all contributing factors to the problems of solid waste disposal. The per capita production of rubbish has increased in the past 50 yr from 2.75 lb per day per person in 1920 to 5.3 lb per day per person in 1968.[1] An even sharper increase in the rate of refuse production is expected in the near future, with a rise from 150 million tons per year to 260 million tons per year predicted for the period 1963 to 1980.[2] These figures and the realization that new materials (for which effective disposal methods have not yet been developed) are contributing to the accumulation of refuse indicate that an imaginative and sophisticated approach is necessary for our future handling of environmental control problems. The practices of the past are not adequate to meet the challenges of today. Their limitations are indicated below in a brief review of current disposal methods.

Sanitary Landfill Practices

Open dumping of solid waste into isolated areas—a method that disregards both long-term effects and aesthetic considerations—is no longer practiced in most metropolitan areas because of strict municipal regulations. However, sanitary landfilling, a more sophisticated version of this approach, is

regarded by the Federal solid waste management program as a currently acceptable method for waste disposal.[3] In this method, waste is deposited in topographically depressed areas (quarries, gullies, etc.)[4] or in trenches excavated by specially designed equipment that is sometimes capable of performing other operations, such as compacting and extruding. The deposit is then covered with a layer of soil that makes the site sanitary. There are several disadvantages in using landfill methods: (1) There are unfavorable economic factors associated with the acquisition of land in municipal areas.[5,6] (2) There is the necessity of reducing the volume of landfill-deposited waste.[7] (3) There are groundwater pollution problems that arise from leaching of refuse constituents in landfill sites.[8] (4) There are combustion hazards due to waste-generated gaseous effluents.[9] Difficulties are also experienced in volume reduction of some polymers because of their inherent flexibility and resistance to permanent deformation by compression. These characteristics of polymers decrease the effectiveness of land utilization and reduce the quality of landfill.[10]

Composting

The conversion of refuse into useful soil conditioners presents an attractive approach to the problem of waste disposal, because utilization of refuse in the terrestrial cycle of biologically transformed compounds has dual effectiveness in that it combines disposal with reclamation. The feasibility of refuse reclamation through composting and the biological digestion of organic matter was proved in the operation of a composting plant in Houston, Texas. This plant converts one-sixth of the city's refuse into soil conditioner by treating waste that is free of metal objects (50,000 tin cans are removed daily) with thickened sewage sludge, grinding the residue, and processing.[11] A similar plant in Johnson City, Tennessee, has also successfully operated in this way.[12]

There are, however, disadvantages in composting municipal waste. Some of these disadvantages relate to the economics of the process (segregating, grinding, and treating refuse components) and to the market possibilities of the product, while others relate to sanitary considerations.[12]

The application of composting techniques to plastics, particularly polyolefins, is rather ineffective because of the pronounced biological inertness of these synthetic materials. However, the possibility of subjecting chemically treated polymers to microorganisms that could utilize the modified material makes the composting approach for the disposal of plastics theoretically feasible. The effectiveness of this approach would depend on the selection of appropriate treatments and microorganisms. Some attention has been given to the microbiological treatment of modified polyethylene in the course of our work. The results are described in the section on the Degradation of Hydrocarbon Polymers.

Incineration

The disposal of municipal refuse by incineration offers a number of advantages, among which is volume reduction of the waste. Benefits are also derived from this method by the destruction of pathogenic microorganisms, although secondary sanitary considerations relating to the potential discharge of air pollutants may reduce the overall usefulness of incineration processes in municipal areas.

A voluminous literature is available on the subject of incineration, and from this only a few representative articles are cited here.[13-18] The unresolved problems of incineration have been discussed in recent technical meetings and engineering conferences. The need for improving the performance of existing and even recently designed incinerator facilities has been emphasized.[19] The desirability of upgrading

instrumentation in municipal incinerator plants[20] and controlling emissions has also been considered.[21]

Effective combustion of waste requires maintenance of proper temperature, time, oxygen admission, and fuel distribution. While low temperatures (below 1,400 F) may result in excessive smoking of burned organic waste, high temperatures (above 2,400 F) are damaging to conventional refractory furnace linings and can also promote reactions that lead to the formation of pollution-causing emissions.

Complete combustion also depends on the maintenance of flame turbulence. This is achieved by the use of stationary or moving grates and rotary kilns. Grates can easily be rendered ineffective when thermoplastic polymers, such as polyethylene, block the air supply by depositing on the grate in a molten mass. The high calorific value of plastics is also responsible for the excessive heat generated during their combustion and the damage incurred by the gratings.

Although incineration of plastic waste, as found in municipal refuse, does not present unusual difficulties at the present level of synthetics in waste (1-2%), engineers in sanitation departments of large cities, such as Chicago, are concerned with the growing amount of plastic materials in garbage, because it is believed that a 3- to 4-percent waste content causes problems in city incinerators. This level may soon be reached because of the increasing use of disposable plastic products and packaging materials.

The potential problems of plastic waste incineration in heterogeneous municipal refuse are closely related to the large differences in the combustion properties of plastic and other waste constituents and to the pollution danger associated with the discharge of hydrocarbon combustion products. The excess oxygen required for adequate combustion of organic polymers is substantially greater than that needed for low-calorific refuse. Consequently, the thermal output (20,000 Btu) exceeds the combustion ratings of municipal refuse (5,000 Btu) by a factor of 3. It is therefore not surprising to find unsatisfactory performance of refuse incinerators in those applications in which a substantial amount of polymers is present in the waste. The manufacturers of incinerators generally claim that the difficulties encountered could be alleviated by redesigning conventional combustion furnaces. They believe that changes in the construction of the furnace, proper stack design, and maintenance of optimum gas-pressure relationships in the incinerator will improve the combustibility of plastics.[22]

A modern incinerator facility operating in a small community in Derby, England, was designed to cope with current waste disposal problems.[23] The plant has a 1,000-cu yd capacity; it operates on two 8-hr shifts and disposes of waste at a rate of 15 tons per hr. Special oxygen supply nozzles were designed to facilitate the combustion of hydrocarbons. Waste gases are passed through mechanical dust collectors before being discharged into the atmosphere through a 130-ft-high chimney. Thus the emission of the particulate materials is limited to the specified level of 0.35 gr per cu ft.

At the present time, the disposal of plastics by incineration does not seriously affect the overall solid waste disposal operation.[24] Continued use of incineration methods in large-scale disposal operations, however, is predicated on the effectiveness of the combustion process and the control of environmental contamination.[25]

DEGRADATION OF HYDROCARBON POLYMERS

The combustion of organic polymers and their substituted compounds to carbon dioxide (CO_2), water, and nonoxidizable products essentially is the ultimate stage in the degradation of these compounds.[26] The simple oxidation products just listed can be

obtained only under ideal conditions.[26] Even incineration results in the formation of measurable amounts of partially oxidized products, which in the combustion of polyethylene may contain more than six carbon atoms in the fragmented chain.

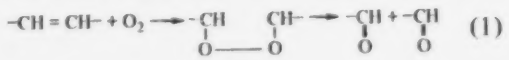
Chain fragments are also obtained in the degradation of polymers by other than combustion methods. For instance, the degradation of high-molecular-weight materials by oxidation, thermal treatment, and radiation can lead to a significant reduction of the molecular size of polymers, thereby making them more accessible for final oxidation in combustion. The changes in mechanical and chemical properties can also promote physical disintegration of plastics and enhance their utilization by microorganisms, thereby facilitating the disposal of high-molecular-weight organic materials. For these reasons, a discussion of the degradation processes of polymers deserves attention.

Structural and Chemical Factors in the Degradation of Polyethylene

The heterogeneous nature of polyethylene, particularly its morphological differences (degree of crystallinity), is largely responsible for localized degradation effects observed in the polymer Polyethylene consists of long hydrocarbon molecules that are tightly packed in a relatively regular array of chains held together by van der Waals forces. The regularity of this array depends on the extent of chain branching, i.e., the presence of side chains (ethyl, butyl) along the main carbon-carbon backbone. Because the chain branches interfere with packing the polymer into a tight structure, the lessened molecular order of branched polyethylene causes lower crystallinity and density. However, branch-separated chains overlap at some points, and the enhanced chain interaction at these points results in the development of microcrystalline (spherulitic) regions that constrain the polymer in a locally ordered network. The overall crystallinity of polyethylene may thus vary from 55 to 99 percent. These morphological differences in polyethylenes influence their responses to chemical reagents.

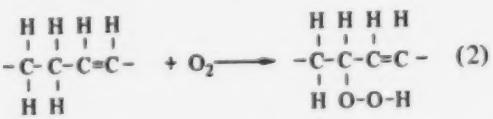
Although the polymer's hydrocarbon nature protects it from corrosive chemicals, the amorphous regions are not immune to chemical attack. The susceptibility of these regions to oxidation is not only a result of the greater accessibility of low-density polyethylene to the oxidizing reagent, but also a result of the greater affinity for oxygen that the branched polyethylene has in comparison to its linear counterpart. Therefore, the chemical effects relating to the presence of substituents on methylene (CH_2-) groups in the main chain of the polymer are equally important in the degradation of polyethylene, because the substituted tertiary carbon atoms present sensitive sites for the formation of free radicals. The free radicals, in turn, are instrumental in propagating the degradation of high-molecular-weight materials, as will be shown later.

The oxidative behavior of polyethylene is also affected by its residual unsaturation, i.e., by the presence of double bonds. Because oxygen (O_2) is capable of adding to the double bond, it may break the polymer chain by the following reaction:



(1)

However, the formation of hydroperoxides is more important than the addition of O_2 to the double bonds. The hydrogen atoms situated on carbon atoms that juxtapose the double bond are very reactive. These allylic hydrogens are most easily engaged in hydroperoxide formation.



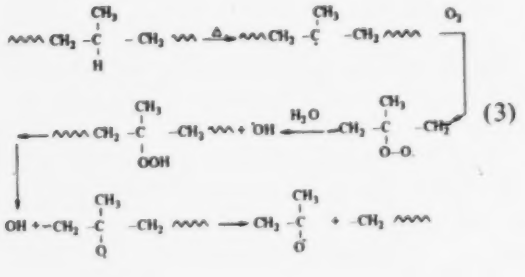
(2)

Because the formation of hydroperoxides governs the chain of events that lead to the oxidative degradation of polymers, the extent of unsaturation in polyethylene has a pronounced influence on the stability of the polyolefin.

The foregoing considerations of morphology, chain branching, and the number of double bonds in polyethylene indicate the different responses of polyethylenes to degradation-promoting influences.

Oxidative Degradation of Polyethylene[27]

Mechanism. The degradation of polyethylene is a result of the simultaneous operation of several types of reactions, each leading to different structural and chemical changes of the polymer. These changes, in turn, produce inordinately large effects on the chemical and physical properties of the substance. In most polymer degradation processes—whether induced by the expenditure of mechanical energy, heat, radiation, or chemical oxidation—degradation takes place through a chain mechanism. This mechanism, which characterizes free-radical processes, provides the unifying concept in the deterioration of high-molecular-weight compounds. In the presence of O_2, polyethylene decomposes by the free-radical mechanism according to the following scheme:



(3)

The initial step of removing a hydrogen and forming a free radical requires the expenditure of a certain amount of energy (heat, radiation, etc.). Then the process becomes self-propagating through the free-radical mechanism. Eventually, scission of the chemical bonds ensues and ketone or aldehyde-terminated molecular fragments are formed. The free radicals generated during degradation are capable of sustaining the decomposition of the polymer by molecular collision and the removal of hydrogen until the reacting chain is eventually terminated by combination of the free radicals, disproportionation of the radical chain, or another mechanism. In polyethylene, the products of ultimate degradation are not predominantly monomer units, i.e., basic chemical entities (ethylene) that constitute the polymer chain, but are organic compounds that present a spectrum of intermediate-size molecules.

The process of bond scission may also be accompanied by the opposite process, cross linking, which leads to an increase in molecular weight and results in the embrittlement of the polymer. The conditions of polyethylene degradation such as chemical environment, temperature, and structural relationships in the polymer largely determine the predominance of either effect. Extensive investigations have been conducted on the oxidative behavior of polyethylene. These investigations include studies of the kinetics of peroxide-induced reactions,[28] effects of branching on the degradation process,[29] and physical changes during degradation.[30]

Temperature Effects. The oxidation of polyethylene is greatly enhanced when the polymer is heated. Above 170 C, the enthalpy of the oxidation process decreases[31] from 33 kcal per mol to a much lower value of 15 kcal per mol at 200 C. This decrease is apparently a result of a change in the rate-controlling step in the oxidation of polyethylene at elevated temperatures. The chemical reaction

between polymer and O_2 occurs so readily at high temperatures that diffusion of the gas into the polymer cannot keep pace with the process; diffusion no longer controls the reaction.

Pressure. The rates of oxidation of polyethylene are proportional to the square root of O_2 concentration for a pressure range of 76 to 760 mm Hg.[32] If this relationship should hold over an extended pressure scale, an increase in pressure by a factor of 100 would increase the reaction rate by a factor of 10. This increase combined with proper temperature control should permit variation of the rate of polyethylene oxidation.

Degree of Subdivision. Because the rate of degradation of polyethylene resulting from exposure of the polymer to a gaseous reagent is to some extent diffusion controlled, the state of polymer subdivision is important in the oxidation process. Studies of the effects of film thickness on oxygen absorption by Ziegler polyethylene indicate a rate thickness proportionality for specimens investigated in the 0.12- to 3.0-mm-thickness range.[33] Although the absorption rate loses its proportionality beyond the 3-mm-thickness limit, a valid relationship is reestablished when the extent of O_2 absorption is followed as a function of surface area rather than thickness.

During combustion, in which oxidative processes are superposed on thermal effects, the rate of reaction of polyethylene is expected to depend on the size and state of subdivision of pyrolyzed products. The foregoing considerations should make clear the importance of physical relationships in the oxidation of polyethylene.

Selected Methods of Polyolefin Oxidation

Although the main prerequisite for the oxidative degradation of polyethylene is the availability of O_2, the oxidation reaction does not proceed at a significant rate when the polymer is exposed to air at normal temperatures. Therefore, from a viewpoint of polyethylene disposal, more severe oxidation conditions are required to produce the desired effects of polymer degradation. Some of these conditions are discussed in the following paragraphs.

Ozonization. The degradative effects of ozone (O_3) on elastomers and flexible polymers—particularly the crack-promoting action of this strongly-oxidizing agent—have received attention in recent years.[34,35] The primary step in the ozonization of polymers is believed to involve chemisorption. Surface attack is enhanced by the thermal energy liberated in the decomposition of O_3, according to

$$O_3 \longrightarrow O_2 + O + 35 \text{ kcal.} \qquad (4)$$

The oxidation of the polymeric bulk, unlike the surface reaction, is diffusion controlled, and the rate of this process greatly depends on concentration. The propagation of a cut in rubber in an O_3 environment is found to require a characteristic energy at the tip of the crack. When this stress is exceeded, the growth of surface cracks occurs spontaneously. Thus O_3 may also be considered a stress-sensitizing agent in stress cracking.

The behavior of polyolefin films on exposure to O_3 has also been a subject of extensive investigations.[36,37] A peroxide mechanism was proposed for the degradation of these polymers. Changes in physical properties, such as melting point, solubility, and viscosity, indicated preferential bond scission for the exposed films. The rate of O_3 attack on polyethylene was greatly enhanced when the reaction was performed at elevated temperatures.[38] However, other workers found that even at room temperature small amounts of O_3, such as those generated in a discharge tube, sufficed to accelerate greatly the oxidative degradation of polyethylene.[39]

Oxidation by Nitrogen Tetroxide. Nitrogen tetroxide (N_2O_4), a gas at temperatures above

21.3 C and a yellow-brown liquid below this temperature, exists in equilibrium with nitrogen dioxide (NO_2):
(NO_2):

$$N_2O_4 \rightleftharpoons 2\,NO_2 \qquad (5)$$

In a manner similar to O_2 and O_3, N_2O_4 oxidatively attacks organic materials through a free-radical mechanism. At temperatures above 100 C, N_2O_4, which under these conditions is largely dissociated into NO_2, reacts with unsaturated groups. The reaction is initiated by hydrogen removal from polyethylene, and the free radicals that are produced combine with NO_2. The activation energy for hydrogen removal is estimated to be 14 to 17 kcal per mol. In its nonionized as well as ionized form,[40] N_2O_4 represents a very reactive agent that can oxidize otherwise resistant polymers.

Crystalline polymers, including high-density polyethylene, are not easily destroyed by oxidation processes; e.g., N_2O_4 degrades high-density polyethylene to a greater extent than low-density and cross-linked polyethylene.[41] This suggests that the dense crystalline areas are penetrated by N_2O_4 and are disrupted by its strong solvating action, or chemical attack. Polyethylene, polypropylene, and especially unsaturated hydrocarbons become embrittled and degrade in the presence of N_2O_4, while silicone rubbers and aromatic polyesters disintegrate upon contact with the oxidizing agent. Even materials such as Teflon are attacked at elevated temperatures by N_2O_4.

The reactivity of N_2O_4 with polyethylene has been studied by infrared absorption spectroscopy.[42] The results show that in the initial stages of oxidation N_2O_4 reacts to form nitration compounds. These compounds consist of nitro groups, nitrate and nitro esters, and carbonyl and hydroxyl groups. At room temperature, NO_2 adds to double bonds, producing dinitro or nitro-nitrite compounds.

Excessively high temperatures are not required for these reactions. Experience acquired at IITRI with N_2O_4 permeation of polyethylene has shown that even at temperatures as low as 75 C, the hydrogen removal occurs quite readily, and chain scission is so extensive that the polyethylene samples lose their coherence. The nitrate esters, as well as carbonyl and hydroxyl groups, are produced by the decomposition of nitrite groups.

The formation of nitrates by the decomposition of polyethylene admits the possibility of utilizing N_2O_4 = oxidized polyethylene in fertilizers and other applications. Decomposition of nitrite esters into carbonyl groups assures the possibility of using this decomposition product in the usual areas in which carboxylic acids are required.

Oxidation by Nitric Acid. Nitric acid (HNO_3), a strong mineral acid that forms an azeotrope with water at a concentration of 68.8 percent, is a very effective oxidizing agent for organic compounds. The formation of nitrates in its reactions with polyols, such as in the manufacture of nitrogylcerine and nitrocellulose, indicate the reactivity of the acid with organic compounds. Nitration can also occur at the carbon atom of a paraffin, in accordance with the following reaction

$$RH + HONO_2 \qquad RNO_2 + H_2O. \qquad (6)$$

The oxidizing capability of HNO_3 is utilized in rocket systems in which it functions as an oxidizer for rocket fuels. The effectiveness of this oxidizer was found to increase with increasing N_2O_4 content. The fuming HNO_3 thus formed causes rapid oxidative degradation of polyhydrocarbons through a free-radical mechanism, as discussed previously. Pronounced changes in the physical properties of polyethylene film were found after exposure to fuming HNO_3. Containers made from this polymer were considered unsuitable for storage of dilute acid.[43]

In addition to its degradative effects on polyolefins, nitric acid treatment of the polymer presents an additional advantage from the viewpoint of plastic-waste disposal. This advantage is the potential use of the acid-treated material as a fertilizer, because partial nitration could provide the nitrogen for assimilation by plants. The modified hydrocarbon would also be more easily attacked by microorganisms, thereby facilitating the ultimate disposal of the plastic. These factors have received consideration in our study.

Thermal Degradation

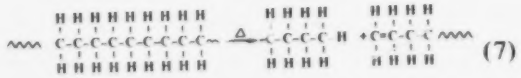
Physical Implications of Chain Scission. The thermal degradation of polyolefins has been a subject of many investigations.[44-47] The relevance of thermal relationships to incineration or combustion processes makes consideration of these relationships particularly desirable in a discussion of polyolefin waste disposal.

The reaction mechanism of the thermal degradation of polyethylene closely follows the free-radical scheme previously described for the oxidative degradation of the polymer. This mechanism applies most strictly to thermal processes that take place in the presence of air, because in the case of air the thermal effects are superposed on oxidation processes.

Polyethylene produces degradation products in a continuous spectrum of intermediate-size molecules. This polymer does not act like the acrylic plastics or even, to some extent, the styrene derivatives—which upon heating are almost quantitatively converted to monomer (the simple structural units that make up the high-molecular-weight material). The polyethylene chain does not unzip in the depropagation step of the degradation process, but rather is randomly broken and reformed into fragments of larger molecular sizes. Thus the monomeric yield for the degradation of polyethylene is very small (0.1% below 200 C), and the rate of volatilization in pyrolysis experiments conducted above 300 C is low (0.4%/min).[48]

These relationships undoubtedly have implications for the combustion of polyethylene, which may relate to the incomplete burning of polyethylene waste and the discharge of low-molecular-weight hydrocarbons along with emitted combustion products and smoke. The proportion of heavier fragments in the products of polyethylene pyrolysis decreases with increasing temperature. Thus the percentage of residual hydrocarbons with chain lengths exceeding an 8-carbon backbone diminishes from 94 percent at 500 C to 41 percent at 1,200 C. This decrease is explained by the competing reactions that take place by random scission in the decomposition of polyethylene.

At lower pyrolysis temperatures formation of large fragments from polymer chains is favored according to the following scheme:



(7)

At higher temperatures fragmentation is more extensive, and the amount of monomer in the products of pyrolysis increases:

(8)

Several problems result from the fragmentation of polyolefins during thermal degradation and combustion. The danger of incomplete combustion and discharge of pollutants is greater for large fragments than for small fragments. Yet the formation of

small molecular fragments would favor complete oxidation of the polymer and result in the dissipation of more heat during incineration. Actually, the effects of carbon-hydrogen and carbon-carbon bond rupture, which are endothermic (heat consuming), counteract the exothermic (heat-dissipating) process of oxidation. Nevertheless, the efficiency of the oxidation reaction determines the heat balance of the process, and the thermal energy expended in bond breaking is outweighed by the heat generated by the thorough oxidation of smaller chain fragments.

Thermochemical Relationships. In considerations of the applicability of incineration to the disposal of plastic waste, it is important to define the thermochemical and thermophysical properties of the materials investigated. Polyethylene packaging film melts into a small bead and burns like a candle when subjected to incineration.[49] A study of the combustible behavior of branched polyethylene (27.7 CH_3 groups per 1,000 carbon atoms) disclosed that the flame maintained by burning a 1-in-diameter rod of this polymer had temperatures of 200 and 700 C at the respective distances of 1 and 2 cm from the surface of the polymer.[50] The combustion products analyzed by mass spectrometry and withdrawn from different sections of the flame indicated that thermal oxidation occurred extensively at 400 to 450 C, although a significant amount of unoxidized hydrocarbons was found among the degradation products at 450 C (Table 2).

The relatively high percentage of incompletely oxidized degradation products of polyethylene emphasizes the potential pollution problem that may be caused by the combustion of polyolefins. The hazards associated with the generation of substantial amounts of CO also deserve attention. These conditions are responsible for the special precautions that fire departments take when combating fires in polyethylene storage areas.

TABLE 2

GASEOUS CONSTITUENTS IN FLAME PRODUCED BY BURNING (450 C) POLYETHYLENE[50]

Gaseous species	Concentration mole (%)
N_2	75.0
O_2	1.4
CO_2	10.3
CO	3.7
CH_4	0.8
C_2H_4	1.6
$n\,C_6H_{10}$	0.8

The problems related to the liberation of excessive heat during combustion of polyethylene waste could be minimized by oxidizing the polymer prior to incineration. The extent to which the heat of combustion of hydrocarbons can be reduced by oxidation or halogenation is indicated by the thermochemical data (Table 3) compiled from published information.[51-53]

The oxidation of propane (C_3H_8) to acetone (CH_3COCH) reduces the heat of combustion of the hydrocarbon by 16 percent. Halogenation has a similar effect, because it results in an 18-percent reduction of the thermal output of completely chlorinated methane. Volatile bromine compounds actually inhibit the combustion of polyethylene, as has been demonstrated in studies with methyl ethyl and isopropybromide combustion-retarding additives.[54] The deliberate introduction of chlorine into hydrocarbons as a means of controlling the thermal relationships of

TABLE 3

HEATS OF COMBUSTION OF PARAFFINS, OXYGENATED HYDROCARBONS, AND HALOGENATED HYDROCARBONS
(Gaseous state, 25 C)

Chloromethane	Oxygenated hydrocarbon	Paraffin	Heat of combustion (kcal/mole)
CH_3Cl			183.2
CH_2Cl_2			164.5
CCl_4			156.8
	$CH_3CH_2CH_2OH$		452.4
	CH_3COCH_3		403.7
		CH_4	191.7
		C_2H_6	341.3
		C_3H_8	488.5
		n-C_4H_{10}	635.4
		iso-C_4H_{10}	633.7
		n-C_5H_{12}	782.0
		n-C_6H_{14}	928.9

polymers must be critically evaluated in view of possible corrosion and pollution problems related to the discharge of hydrogen halides.

Differences in thermal response were also noted in studies on high- and low-molecular-weight polyethylene.[55] The rates of polymer degradation at 376 C were 0.078 and 0.011 percent for polyethylene with respective molecular weights of 16,000 and 23,000. Linear polyethylene also had a higher activation energy for thermal degradation (74 kcal/mole) than the branched polymer (63 kcal/mole). This energy difference substantiates the previous observations on the greater stability of unbranched polyethylene and the degradation of low-molecular-weight chain fragments.

Other Methods of Polymer Degradation

Mechanical Effects. The degradation of polymers by mechanical means has long been established in studies on masticated rubber.[56] In this degradation, formation of free radicals in the process of mechanically induced bond scission leads to interaction of free-radical chains with the oxygen that is present in a normal environment, thereby causing permanent disruption of the polymer structure. Shear degradation of polymers takes place in a nonrandom fashion, as is indicated by a sharp rather than broad molecular-weight distribution of the degradation products.[57] The preferential fracture of polymer chains at selected sites along the chain has been attributed to the

localized stress conditions in the polymer when subjected to tensile loads. Consideration of stress conditions in a chain-entangled polymer system demonstrates the existence of maximum stress at the center of polymer chains.[58] This condition explains the narrow molecular-weight distribution of mechanically degraded polymers.

The degradation of polymers by mechanical methods has been generally criticized for its undesirable although often unavoidable effects, and several approaches have been utilized to inhibit these undesirable effects. However, when these effects are beneficial, it is also possible to enhance the process by the use of selected, degradation-promoting catalysts. The applicability of this approach will be discussed later.

Ultrasonic Degradation. The degradation of polymers by ultrasonic methods involves a physical phenomenon slightly different from that which is operative in the shear degradation of plastics. In this degradation, the stresses that are created within the macromolecule by the collapse of a cavity produce a shock wave that radiates from the cavity.[59,60] Pressures of the order of 1,600 atm may develop, thus leading to the disintegration of polymer. The process involves bond scission at preferential sites and results in a relatively narrow distribution of the molecular weights of the degradation products, analogous to the distribution obtained in polymers subjected to shearing forces during mastication. Usually there is obtained a critical average molecular weight that cannot be further decreased by prolonged exposure to ultrasonic energy. For polystyrene, this molecular-weight limit is 30,000, regardless of the initial molecular weight of the parent polymer.

Although ultrasonic methods of polymer degradation have many attractive features, the cost involved (power requirements and equipment cost) may be too prohibitive to justify the use of this approach in the disposal of waste.

Stress Cracking. A variant of the mechanically induced deterioration of plastics, particularly of polyethylene, is presented in stress cracking. This phenomenon is defined as the failure in the surface-initiated brittle fracture of a polyolefin part under polyaxial stress, when the part is in contact with a stress-sensitizing gaseous, liquid, semisolid, or solid medium.[61]

The stress state has an important part in environmental stress cracking. High uniaxial stresses cause most polyolefins to flow excessively and thus change their physical characteristics. However, biaxial stresses allow high-energy storage without excessive deformation, and, under these conditions, environmental attack rapidly leads to embrittlement and fracture. Environmental stress cracking may thus induce failure in polyethylene at stresses much lower than its ultimate strength. The susceptibility of polyolefins to stress cracking depends on load conditions, the nature of the stress-sensitizing medium, and the molecular weight distribution of the polymer. Polyethylenes with a narrow molecular weight distribution were found to exhibit superior resistance to environmental stress cracking.[62]

An effective crack-inducing sensitizer was found for polyethylene in a surface energy-reducing organic compound, Igepal (General Aniline and Fiber Co.). The time-failure stress relationship for polyolefins subjected to Igepal solutions is shown in Figure 1. The catastrophic onset of fracture in polyethylene after a 10-hr exposure to the crack-promoting environment indicates the potential applicability of this method for the enhancement of polymer degradation.

Radiation Effects. Photolysis. The degradative influence of solar radiation on synthetic polymers, often manifested in visual (color) changes, is well known. Photolytic processes involving bond rupture within the backbone of the polymer chain require a minimum energy expenditure equivalent to that of the C-C bond strength. Since this energy is of the

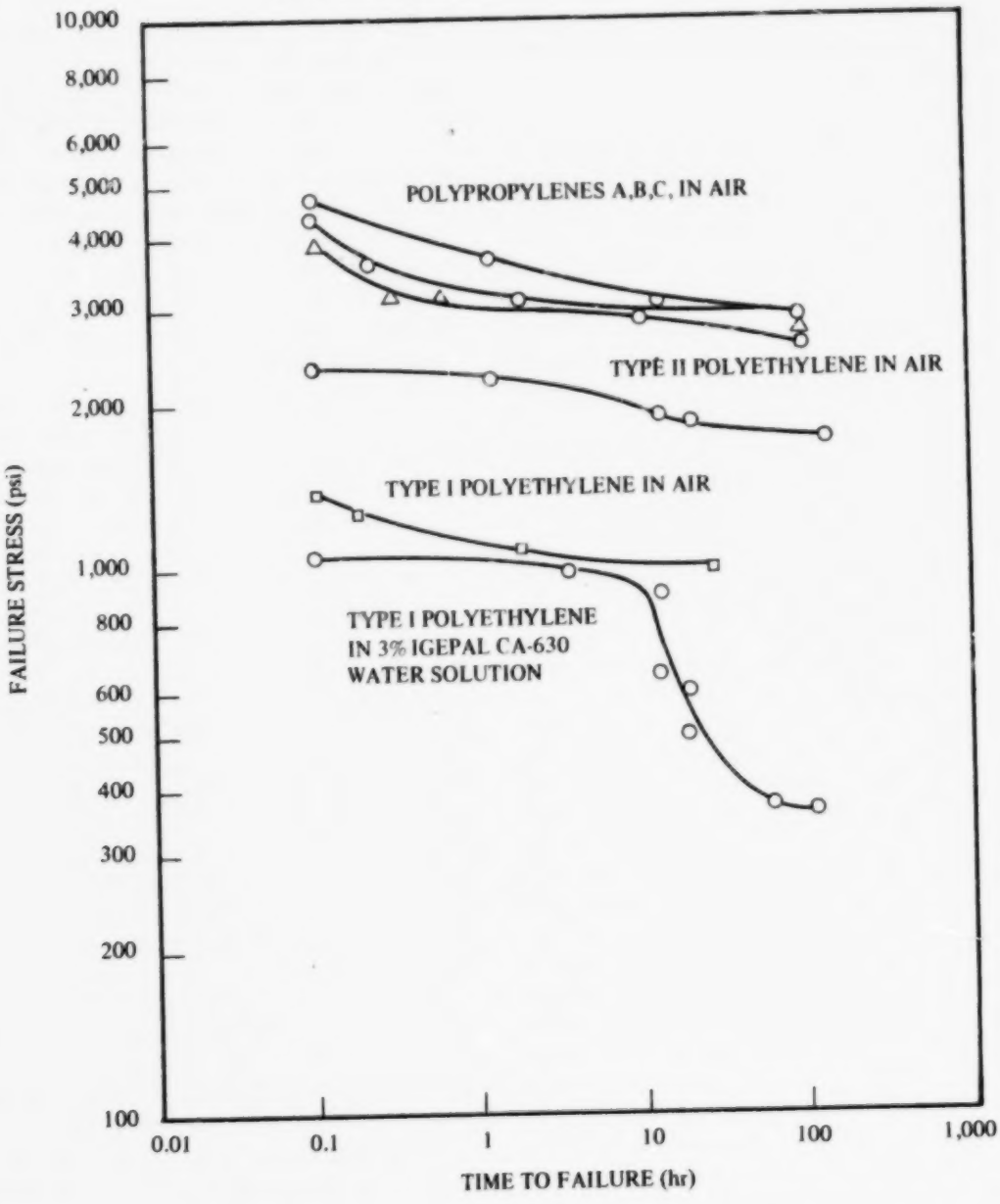


Figure 1. Environmental stress-cracking behavior for some olefin polymers.

order of 80 to 100 kcal/mol, it is not surprising to find a radiation threshold from 3,000 to 4,000 A (ultraviolet range) beyond which photodegradation of organic polymers does not occur (visible range). Thus radiation in the ultraviolet range is most injurious (highly degradative) to high-molecular-weight organic compounds.

Photolytic bond scission is the initial step of polymer degradation which leads to the formation of free radicals that react with the polymer chains to produce further fragmentation through the free-radical mechanism of a chain reaction. In the presence of oxygen, the photoinitiated degradation process continues by the hydroperoxide scheme of the oxidative degradation process.

The principles and operative considerations in photochemical processes, including photodegradation, were recently the subject of a symposium. New, powerful, ultraviolet-light sensitizers for the cross linking of polyethylene plastic were discussed.[63] The old function of the sensitizer, long performed by uranyl salts and benzophenone, has been augmented by other agents such as anthrone. Because of its aromatic substituents, anthrone does not take part in coupling reactions and therefore gives a higher quantum yield than benzophenone. However, the use of ultraviolet sensitizers to promote the degradative interaction of plastic and oxygen is sharply limited by the relative impenetrability of the polymer by some forms of radiant energy. Film sections ranging from 0.001 to 0.004 in. are affected by ultraviolet radiation; but films of greater thicknesses require extended periods of exposure before they exhibit noticeable signs of degradation.

High-Energy Radiation. The great advantage of high-energy radiation is its ability to penetrate deeply into polymer sections. This penetration allows chemically disruptive influences to manifest themselves within coarse plastics.

In radiolytic methods, higher radiation energies than those obtained from ultraviolet sources can induce rapid deterioration of polymers. Thus ionizing radiation provided by Co^{60} predominantly produces chain scission in some polymers, such as alpha-methyl styrene, while in others, such as polyethylene, it causes bond scission and cross linking. The relationship between the molecular parameters of polymers and their response to ionizing radiation applies to scission and cross-linking processes.

The degree of crystallization, chain branching, and the nature of substituents influence the extent of degradation. In radiation-induced cross-linking, the polymer can form a rigid, three-dimensional network, which in the extreme case may form an embrittled material that could fracture with the expenditure of relatively little mechanical energy. The effectiveness of radiation-induced changes in polymers depends on thermal conditions and the nature of the environment in which the material is subjected to radiation. This thermal dependence is not surprising. An abrupt increase in radiochemical energy at the glass transition point could be expected, because the interaction of free-radical chains above and below this point could occur by different processes, such as disproportionation and recombination.

Degradation of polymers by radiolytic methods merits attention for facilitating the disposal of polyolefin waste. However, the practical implementation of this approach requires thorough investigation.

Biodegradation. The microbiological degradation of organic compounds, including polymers, has been investigated for many years, particularly the adverse effects of biological action on the durability of synthetic fabrics and insulating materials.[64,65] More recently, attention has been given to the positive effects of microbiological degradation of high polymers, specifically in studies of waste disposal.[66-68]

Transformations of paraffins, petroleum, and other aliphatic hydrocarbons are significant in the terrestrial cycle of carbon, because they are constituents of plant tissue. Microflora decompose the naturally occurring aliphatic hydrocarbons, but the higher-molecular-weight homologs are not so easily attacked by microorganisms. However, acid-fast mycobacteria, *Nocardia*, *Pseudomonas*, *Streptomyces*, *Desulfovibrio*, *Corynebacterium*, and some cocci and fungi have been found to attack hydrocarbon polymers.[69]

Vinyl plastics appear to be particularly sensitive to *Alternaria*, *Aspergillus*, *Penicillium*, *Rhodotorula*, *Streptomyces*, and *Trichoderma*. However, because vinyl polymers are generally used in a plasticized state, the plasticizer rather than the polymer might provide the nutrient for the microorganisms. Plasticizers are susceptible to fungal attack—glycol derivatives being more readily utilized by microorganisms than derivatives of phthalic acid. Generally, the growth rate of fungi on plasticizers varies with the test organism used. Thus, conclusions concerning fungal resistances of aromatic plasticizers based on the response of a single microorganism are grossly misleading.

The deterioration of polyvinyl chloride films subjected to the influence of soil microorganisms for 5 years in underground exposure studies disclosed marked biological action. The embrittlement and loss of elongation of these films indicate partial removal of the plasticizer. However, the observed increase in the concentration of hydroxyl and carboxyl groups suggests that bacterial and fungal organisms directly attack the polymer.

For waste disposal, the resistance of some polymers to biodegradation could be greatly reduced by chemical modification of the polymer prior to its exposure to microorganisms. This modification particularly applies to polyethylene whose biological inertness could be overcome by appropriate chemical sensitization.

EXPERIMENTAL INVESTIGATIONS

The possibility of facilitating the disposal of polyolefins by the previously discussed methods of polymer degradation suggested the desirability of determining the applicability of some of these methods to polyethylene waste. Accordingly, concurrent with the literature survey on the practices of plastic-waste handling, an experimental study was initiated to investigate the merits of selected approaches to promote degradation and ultimate disposal of hydrocarbon polymers. Particular consideration was given to the effects of gaseous and liquid oxidants on thermal properties of polyethylene, the influence of ultraviolet and high-energy (gamma) radiation on the thermal and mechanical behavior of the polyolefin, and the effects of chemical treatment on the biological response of the modified material. These studies are described in the following paragraphs.

Materials

Polyolefins. In most studies, commercial, low-pressure polyethylene with a molecular weight of 40,000 to 60,000 (Alathon 20, E. I. du Pont de Nemours & Co.) was employed. This material is widely used in extrusion and blow-molding processes and was therefore selected for our investigations. In preliminary characterization studies, several other polyethylenes were used. These polymers differed in molecular weight and structure. They included a low-molecular-weight material (AC-6, molecular weight 2,000, Allied Chemical Co.), an extrusion-grade, low-melt-index polymer (Alathon 10, molecular weight 30,000), and two high-molecular-weight experimental

compounds (molecular weight 200,000)—one having a linear structure (No. 46892, Phillips Petroleum Co.), and the other having a branched-chain configuration with seven side chains per 1,000 carbon atoms (No. 46894, Phillips Petroleum Co.). Polyethylene was used when possible in pellet form (1/8-in. diameter discs) or as powder sieved through a 20-mesh screen. For studies on larger-size specimens, samples 1/2-in. diameter x 10 in. were prepared by extrusion.

Reagents. The chemical compounds used as reagents, or promoters, for the degradation of polyethylene were reagent-grade chemicals purchased from commercial sources. These chemicals included the following sensitizing compounds: benzoin, 2,2′-azobis (2-methylpropionitrile), cobalt nitrate ($Co(NO_3)_2$), cobalt molybdate ($CoMoO_4$), manganese nitrate ($Mn(NO_3)_2$), cobalt chromate ($CoCrO_4$), and iron chloride ($FeCl_3$). Among the oxidizing reagents used in this study were the following: nitric acid (HNO_3), red fuming nitric acid (RFNA), nitrogen tetroxide (N_2O_4), benzoyl peroxide (BzO_2), chlorine (Cl_2), sodium hypochlorite (NaOCl), and sodium chlorate ($NaClO_3$). Pure oxygen (O_2) and a mixture of O_2 and ozone (O_3) (5.5%) were used in thermal oxidation studies on polyethylene.

Methods

Experimental investigations of the effects of selected treatments and reaction conditions on the properties of polyethylene were based on thermal, mechanical, and analytical measurements. These measurements included differential thermal analysis (DTA), calorimetry, determination of stress-relaxation and stress-strain behavior at high and low rates of loading, infrared spectrophotometry, and viscometry. Analytical and bichemical methods were used to determine chemical changes in treated polymers and changes in their biological responses.

Differential Thermal Analysis. Differential thermal analysis is a useful method for investigating and comparing the reaction rates and energetics of high temperature processes under dynamic conditions. Reversible decomposition-oxidation reactions can be followed during the cycles of heating at elevated temperatures and subsequent cooling at constant heating or cooling rates. In the DTA experiments, the temperature difference, ΔT, between the sample under investigation and an inert reference, Al_2O_3, is measured as a function of temperature during heating or cooling. Reactions such as decomposition and phase transition, which involve absorption of heat by the sample, are indicated by endothermal bands in the downward direction on the differential thermogram, and reactions such as in oxidation, condensation, and crystallization, in which heat is liberated, are indicated by exothermal bands in the upward direction of the differential thermogram.*

The temperature range of 25 to 700 C was scanned at a rate of 10 C per min. Primary consideration was given to the changes in the thermal response of polyethylene after exposure to different degradation-promoting treatments. To assess more critically the changes in the thermal behavior of modified polymer, areas under the DTA curves were integrated for the 200-to-450 C range by using a planimeter, and the thermal outputs were compared for specimens that received different treatments.

Calorimetry. The heats of combustion of polyethylene before and after treatment were determined by conventional calorimetric methods as a corollary of DTA measurements. The measurements were performed with a Parr bomb calorimeter at a pressure of 25 atm O_2 on samples that weighed approximately 0.5 g each. The thermal changes after ignition were followed for 15 min. The heat dissipated

*A model KA-2H DTA apparatus, manufactured by the R.L. Stone Co. was used.

during combustion of the specimen was determined from the maximum thermal increase of the system, and its heat capacity was determined after the usual corrections were applied for the formation of reaction products other than CO_2 and water. The specimens were compressed into a pallet whenever the polyethylene disintegrated during exposure to degradation-promoting conditions, in order to permit a better correlation for the data obtained on treated polyethylene.

Mechanical Properties. The effects of chemical treatments on mechanical properties of Alathon 20 were investigated in compression tests designed to determine the crushability of modified polymer. In these tests, polymer specimens (1/8-in.-diameter disks) were subjected to the crushing force of a steel plunger descending on the sample at a rate of 0.5 in. per min. Lateral displacement of the disk was eliminated by the use of a concave hemispherical holder. Load-deformation diagrams were obtained on the Instron testing machine. The decay of the force of the impressed load (at constant strain) was also followed for specimens that were compression loaded to 30 lb at a rate of 0.5 in. per min. The decay of the initially impressed force reflected the extent of internal damage of the crushed specimens.

The changes in the structural integrity of polyethylene after exposure to degradation-promoting conditions were also investigated by mechanical test methods involving the rapid compression of cylindrical specimens, 1/2-in. in diameter and 1/2-in. in length. Measurements were performed on a Plastechon high-speed testing machine in which the samples were compressed at a rate of 4,000 in. per min.

Infrared and Viscometric Studies. Treated samples were subjected to infrared spectroscopic measurements and viscometric studies to determine the extent of changes in chemical properties that resulted from specific treatments of polyethylene. Whenever possible, infrared measurements were performed on films prepared at elevated temperatures from polyethylene samples that were powdered by compression molding. Mulls with Nujol oil or Kel-F fluorocarbon were prepared when the treated polymer could not be compressed or cast into a film. The main emphasis in infrared spectroscopic investigations was placed on the chemical changes resulting from oxidation or nitration of the treated polyethylene.

Corollary studies on changes in polyethylene after treatment were conducted by viscometric measurements. The viscosity of polyethylene in xylene was determined at 80 C for solute concentrations ranging from 0.1 to 5 percent. The exact concentration of the solutions was determined by gravimetric methods. The effects of selected, degradation-promoting treatments on viscosity relationships were assessed from plots of relative viscosity against solute concentration. An Ostwald viscosity pipette was used for the measurements.

Analytical Measurements. The effectiveness of HNO_3 treatments for polyethylene was determined by analytical measurements of the amount of residual nitrogen in treated samples. The procedure, based on micro-Kjeldahl techniques, involved heating a 30-mg sample for 12 hr in a 30-ml Kjeldahl digestion flask containing 1.3 g of potassium sulfate (K_2SO_4), 40 mg of mercuric oxide (HgO), and 2 ml of concentrated sulfuric acid (H_2SO_4). A 2-mil aliquot of the digested sample was removed from the flask after dilution to 50 ml. This aliquot was further diluted with 3 ml of 2 N sodium hydroxide (NaOH) and 2 ml of a color reagent containing 4 g of potassium iodide (KI), 4 g of mercuric iodide (HgI_2), and 1.75 g of ghatti gum. The intensity of the developed color was determined after 15 min by a photometer at a wavelength of 490 mμ. A calibration curve obtained with known concentrations of ammonium sulfate ($(NH_4)_2SO_4$) permitted the quantitative

determination of the residual amount of nitrogen in the samples.

Biological Studies. The susceptibility of chemically treated polyethylene to biodegradation was investigated by exposure of test specimens to selected microorganisms in an inoculated agar system containing 1 percent (by weight) of dispersed material. The organisms used were *Aspergillus niger, Aspergillus flavus, Aspergillus versicolor, Penicillium funiculosum,* Trichoderma, and *Pullularia sullans.* Studies were later conducted on strains of *Pseudomonas aeruginosa.** The composition of the suspension medium is given in Table 4.

The agar system was sterilized and the pH of the system was adjusted to 6.2 by an addition of 0.01 N NaOH. Tests conducted at room-temperature incubation (25 C) at a relative humidity of 95 percent comprised a modified ASTM D1924-63 procedure in fungal utilization studies.

TABLE 4

SUSPENSION MEDIUM

Ingredient	Concentration (g/1)
KH_2PO_4	0.7
K_2HPO_4	0.7
$MgSO_4.7\ H_2O$	0.7
NH_4NO_3	1.0
NaCl	0.005
Agar	15.0

Experimental Results

Differential Thermal Analysis Studies. Preliminary investigations of the thermal response of polyethylenes differing in molecular weights and structures were performed by DTA methods on a low-molecular-weight polymer (2,000) and high-molecular-weight polyethylenes(200,000) with linear- and branched-chain configurations. The thermograms obtained for these materials at high instrument sensitivity are shown in Figure 2. The low-molecular-weight polymer is the least thermally stable, with its melting endotherm having a peak at 106 C, while the branched and linear polymer specimens have peaks at 117 and 137 C, respectively. The thermal degradation of the low-molecular-weight hydrocarbon also occurs earlier than that of the high-molecular-weight material. The oxidation exotherm is much more pronounced for the linear polymer than for its branched counterpart. The smaller amount of heat evolved during heating of the branched polyethylene is apparently a result of the concurrently occurring degradation and oxidation processes. Because of the absence of tertiary carbon atoms, the linear polymer does not undergo substantial degradation at lower temperatures. The thermal plateaus for all polymers tested above 570 C indicate complete combustion of the polyolefins at this temperature. These data confirm the dependence of thermal relationships on the intrinsic properties of ethylene polymers.

Alathon 20 was exposed to N_2O_4, RFNA, O_3 and Cl_2 to study the effects of chemical treatment on the thermal behavior of polyethylene. The treatment with N_2O_4 was initially conducted at -10 and +20 C, with samples exposed to the reagent for 5 and 20 hr. The greater tendency of the polyolefin to disintegrate when treated with N_2O_4 at the higher temperatures suggested a need for a further increase in temperature to ensure the completeness of the reaction within a shorter time. Thus Alathon 20 was exposed at 80 C to the reagent in a pressure-withstanding

*Strains ATCC 10145 and QMB 1468 were obtained from American Type Culture Collection and the U.S. Army Natick Laboratories, respectively.

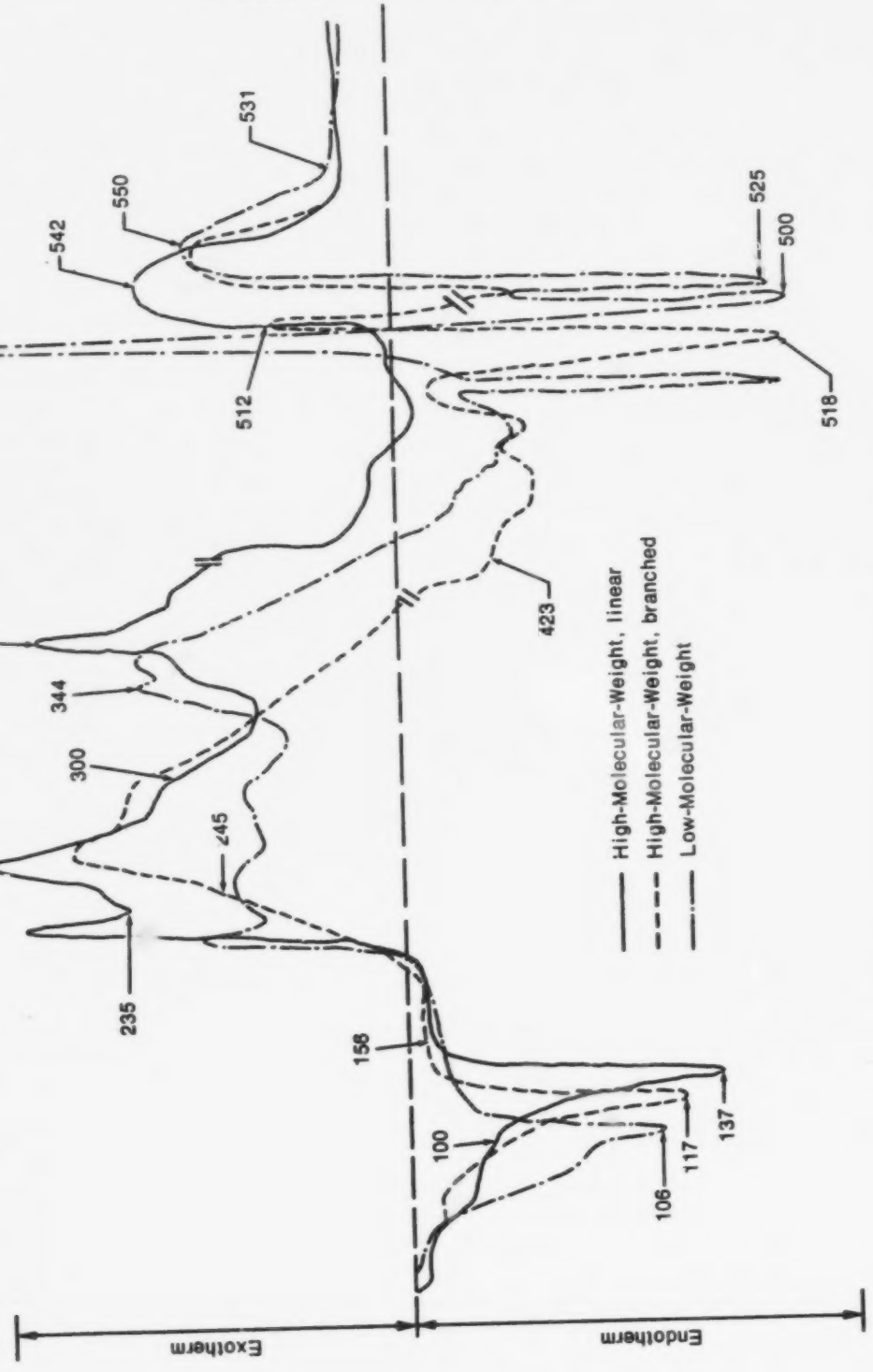


Figure 2. Differential thermograms of different polyethylenes.

reaction vessel. Unfortunately, under these conditions the reaction occurred violently after 1 hr, causing an explosion that injured one of the workers. Treatment of polyethylene with RFNA at 80 C did not present the reaction problems encountered with N_2O_4, and this method was substituted for the more sensitive and hazardous treatment with N_2O_4.

Chlorination involved a 5-hr exposure of 100 g of polymer in a sample-holding glass tube to a stream of Cl_2 that entered the tube at a rate of 1 liter per min. To enhance the reaction, the tube was heated in a furnace at 80 C. Difficulties in maintaining a constant reaction temperature below the melting point of the polymer were eliminated by a thermocouple control unit that was used with an auxiliary heater.

The possibility of degrading polyethylene by exposure to O_3 was investigated in a parallel experiment in which the polymer was subjected to oxygen containing 5.5 percent O_3 at a flow rate of 0.5 liter per min. The O_3-enriched environment flushed through the test specimens was obtained from a commercial O_3 generator. To enhance the reaction, a temperature of 40 C was maintained during the exposure of Alathon 20 to the oxidizing environment.

The thermograms obtained for N_2O_4- and RFNA-treated polyethylene after a 5-hr exposure are shown in Figure 3. As indicated, N_2O_4 appears to enhance the degradation of the polymer to a greater extent than RFNA during the 5-hr exposure. A shift toward lower melting temperatures is noticed for RFNA- and N_2O_4-treated polyethylene in comparison with the parent material. Also, the chemically treated polyolefin has terminal endothermal peaks (associated with decomposition) shifted toward lower temperatures than the peaks of the unexposed standard. Early thermal decomposition as well as oxidation occurs at lower temperatures for N_2O_4- exposed polyethylene than for its RFNA-treated counterpart. These data emphasize the effectiveness of the N_2O_4 treatment in inducing changes in the polymer in short-duration exposure tests (Table 5).

The changes in the differential thermograms of polyethylene after 5- and 10-hr exposures to RFNA at 80 C are presented in Figure 4. The longer duration of exposure results in a reduction of the amplitude of the exothermal peak in the 450-to-500 C temperature range. The most significant change in the thermal response of treated polyethylene in comparison with the untreated material occurs in the initial stages

TABLE 5

THERMOANALYTICAL DATA FOR TREATED AND UNTREATED POLYETHYLENE

Property	Temperature, C		
	Treatment		
	None	RFNA*	N_2O_4*
Melting point	109	103	103
Exotherm	205-375	190-360	190-325
Early decomposition	375-475	350-450	325-425
Terminal endotherm A	515	500	490
Terminal endotherm B	530	525	512

*Five-hr exposure at 20 C.

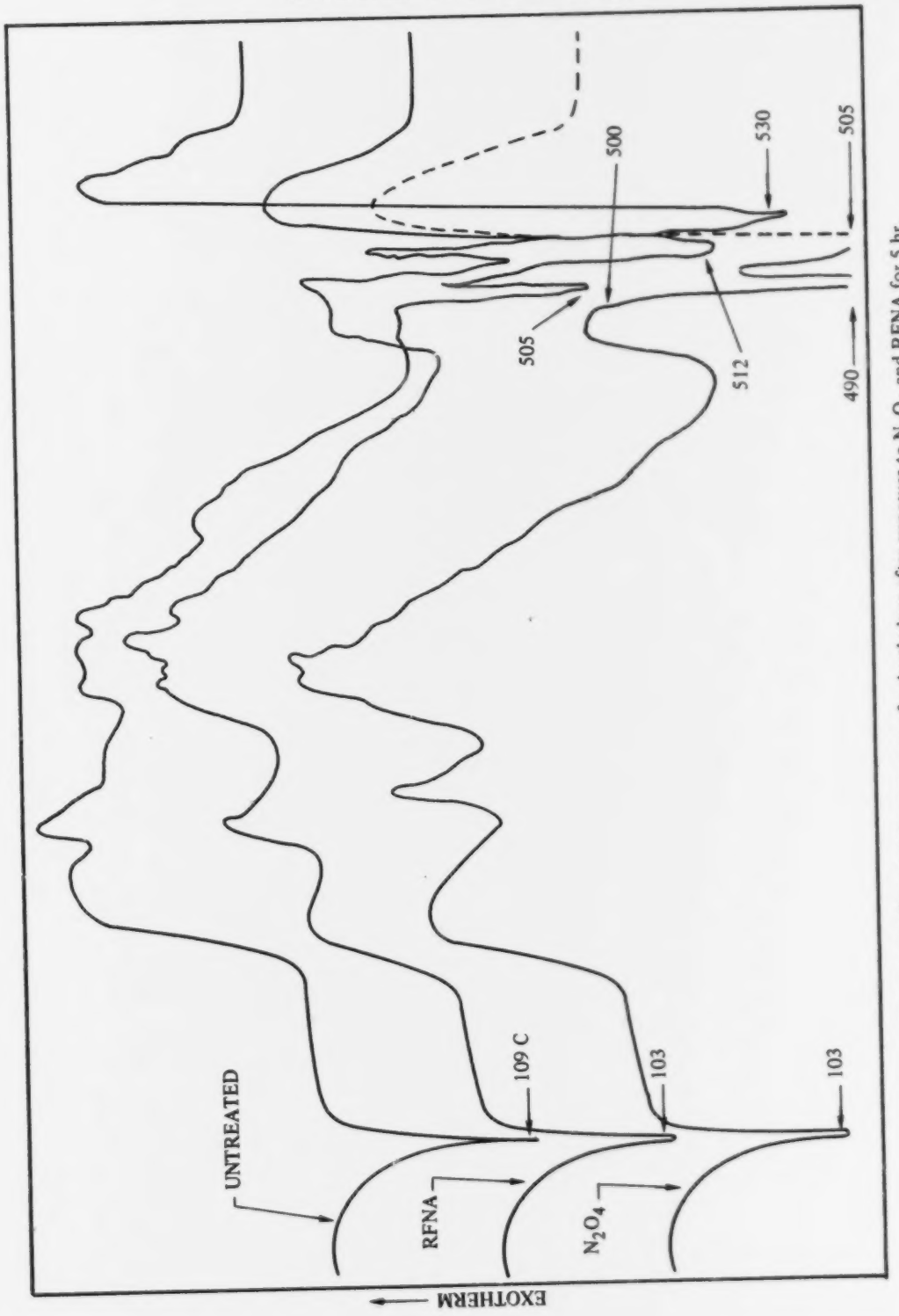


Figure 3. Differential thermograms of polyethylene after exposure to N_2O_4 and RFNA for 5 hr.

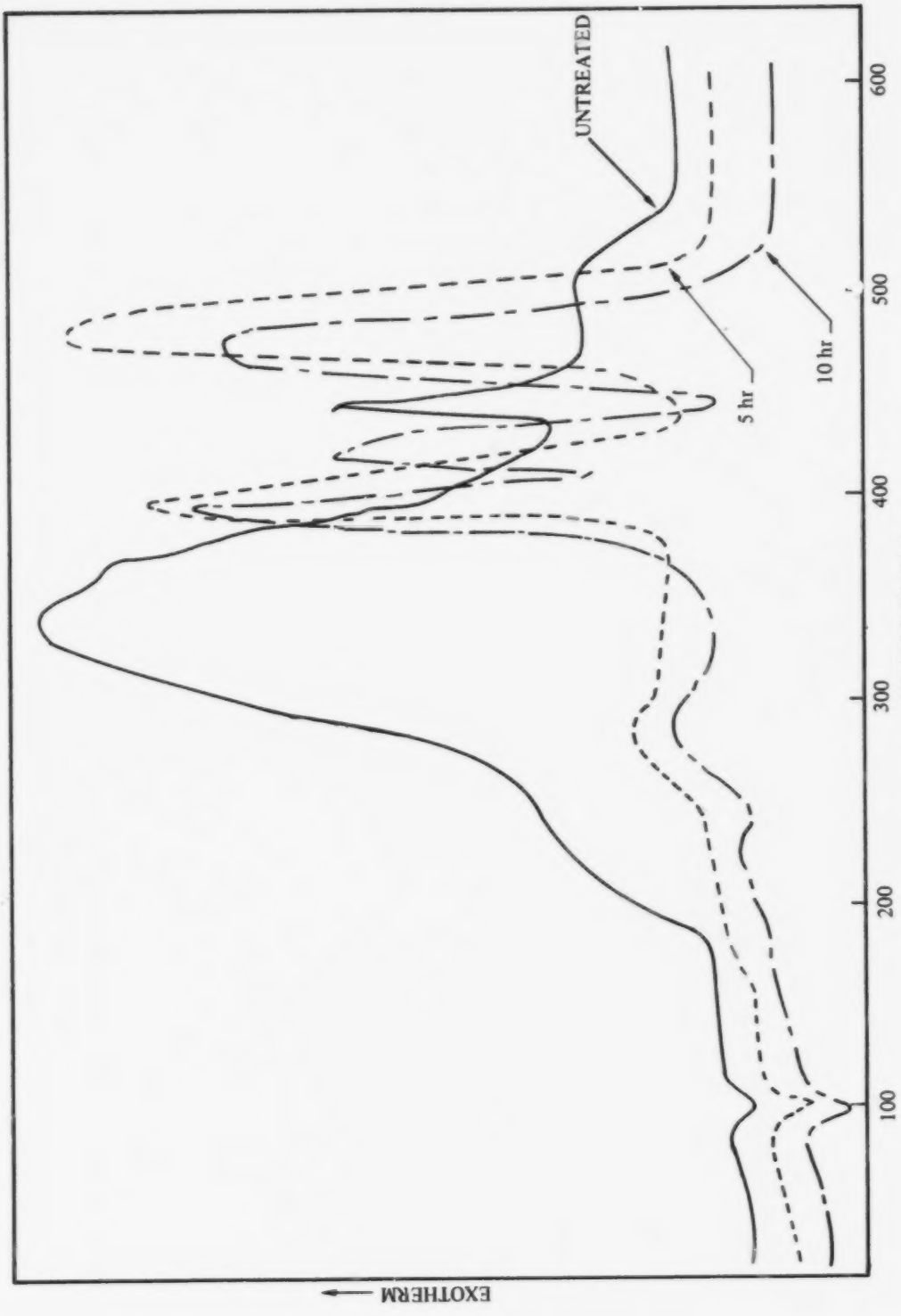


Figure 4. Differential thermograms of RFNA-treated polyethylene.

of oxidation, when the early exotherm in the 200-to-450 C range is greatly reduced after RFNA exposure. Comparing the effectiveness of different treatments shows that chlorination and RFNA treatment decrease the total exotherm of the polyolefin to a significant extent, while ozonization influences the thermal properties of polyethylene to a lesser degree (Figure 5). Integration of the areas under the DTA curves indicates a 23-percent reduction in the thermal response of ozonized polyethylene in comparison with 43 percent for the RFNA-treated polyethylene (Table 6). The increasing ratios of the total/initial areas with increasing exposure to the oxidizing media (with the exception of the 5-hr RFNA treatment) suggest that polyethylene undergoes substantial oxidation when treated with RFNA, and that the oxidation products obtained require exposure to higher temperatures to be fully oxidized by thermal methods.

In additional studies of the thermal behavior of chemically treated or sensitized polyethylene, Alathon 20 was exposed to different reagents. Benzoyl peroxide, 2,2'-azobis(methyl)propionitrile, and benzoin were used in a 10 percent toluene solution (10% solute) in which polyethylene was heated at 80 C for 20 hr to acquire a desired degree of sensitization to further oxidative or photolytic degradation. The preference for toluene as solvent was suggested by its swelling action on polyolefins and the resulting increase in polymer absorptivity of the sensitizers. After the 20-hr treatment, the polymer specimens were removed from the treating solution and were placed in one layer on aluminum dishes. These dishes were introduced into an ultraviolet (UV) irradiation facility in which they were kept for 70 to 96 hr under an AH-6 lamp with an irradiance of 110 mv per cm.[2] The irradiated samples were subsequently tested for changes in thermal properties.

TABLE 6

THERMAL DATA FOR CHEMICALLY TREATED POLYETHYLENE

		Integrated area under DTA curve*		Relative exotherm	
Specimen	Treatment	200-450 C range	Total	Control	Total: 200-450 C range
Alathon 20	None	0.425	0.605	1.0	1.4
Alathon 20	O_3	0.394	0.525	0.867	2.2
Alathon 20	Cl_2	-	0.351	0.580	-
Alathon 20	5-hr RFNA	0.163	0.356	0.588	3.6
Alathon 20	10-hr RFNA	0.177	0.347	0.573	3.2
Alathon 20	20-hr RFNA	0.148	0.380	0.628	4.2

*Arbitrary units.

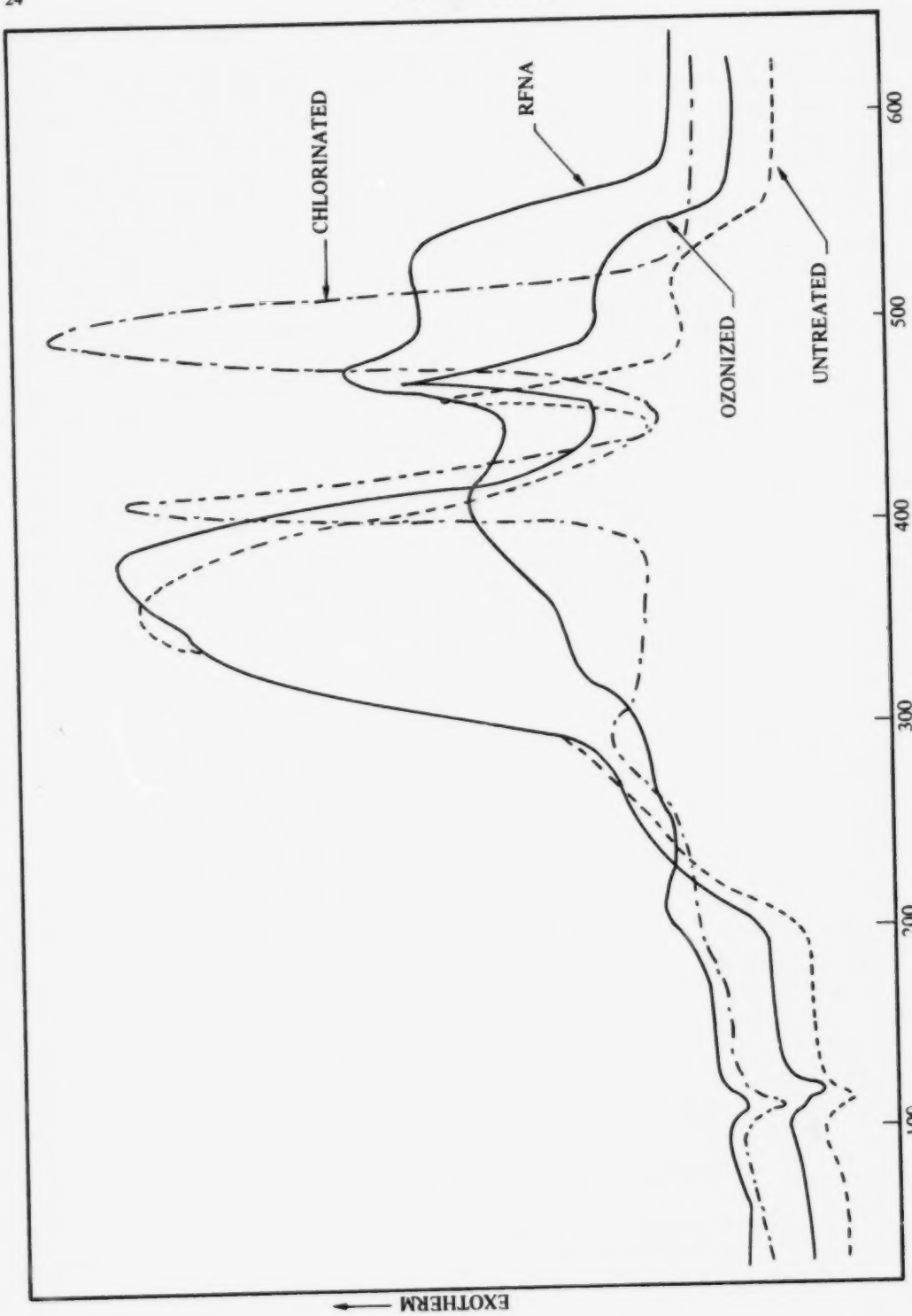


Figure 5. Differential thermograms of polyethylene after treatment.

Concurrently with the photodegradation studies, polyethylene samples were also exposed to pure O_2 at 80 C. Prior to this exposure the polymer was treated with benzoyl peroxide, or $FeCl_3$ catalyst, in a 10-percent methanol solution (10% solute). The oxidation apparatus essentially consisted of five Pyrex glass tubes connected in series to an oxygen tank. Each tube, containing 10 g of polymer, was flushed with O_2 at a rate of 0.5 l/min. The tubes with the samples were partially immersed in a heating bath that was maintained at 80±2C. After a 20-hr exposure to O_2, the specimens were subjected to DTA.

In corollary experiments, polyethylene pellets were exposed to high-energy radiation in a Co^{60} facility. The specimens received increasing doses of gamma radiation (100, 200, 400 megarads) and their chemical and mechanical properties were investigated. The thermal responses of the treated samples are summarized in Table 7. Closer analysis of data suggested greater, although not unusual, thermal effects in samples that were subjected to oxidation and UV irradiation. The ratio of the total to initial heat output of benzoyl-peroxide-sensitized polyethylene is greater after O_2 treatment than after UV irradiation. This increase could suggest the possibility of preferential bond scission of the UV-treated polymer, because its fragmentation, followed by oxidation, would tend to decrease the exothermal ratio. In the absence of degradation-promoting catalysts, gamma radiation at the 200-megarad level

TABLE 7

DTA DATA FOR TREATED POLYETHYLENE

Treatment	Integrated area under DTA curve (arbitrary units)		Relative exotherm	
	200-450 C range	Total	Specimen control	Total initial range
Benzoyl peroxide + O_2	0.160	0.220	0.743	1.375
Benzoyl peroxide + UV (96 hr)	0.178	0.184	0.622	1.030
Benzoyl peroxide	0.204	0.258	0.872	1.260
$FeCl_3$, + UV	0.182	0.222	0.750	1.220
$FeCl_3$, + O_2	0.224	0.316	1.067	1.411
Benzoin + UV (70 hr)	0.180	0.190	0.642	1.060
2,2'-azobis(methyl)propionitrile + UV	0.186	0.240	0.811	1.290
Co^{60} (200 megarads)	0.200	0.269	0.902	1.345
Co^{60} (400 megarads)	0.188	0.218	0.736	1.160

appears to favor cross linking of the polymer. The cross linking was suggested not only by the higher exothermal ratio of the irradiated polyolefin, but also by the apparent interactability of the modified polymer at temperatures exceeding 150 C.

The differential thermograms obtained for polyethylene subjected to oxidation after treatment with sensitizing compounds of selected transition elements (Co, Mn, Cr, Mo) generally showed an increase in the areas under the DTA curves for the high-temperature/total-temperature range in comparison with unsensitized polymer, thus indicating the relative effectiveness of the treatments. However, these treatments did not significantly change the overall thermal response of polyethylene, as was also substantiated by calorimetric measurements. Greater effects were observed for Alathon 20 after a 3-hr exposure to phosphorus trichloride (PCl_3) at 60 C. The results are shown in Figure 6. In order to obtain information about the effects of treatments on the behavior of polyethylene during incineration, the thermoanalytical studies were supplemented by heat-of-combustion measurements. The data derived from these studies are discussed in the following paragraphs.

Calorimetric Measurements. The initial indications of a reduced thermal output of RFNA-treated polyethylene suggested a need to determine the heat of combustion of the modified polymer. The data obtained indicated a progressively decreasing thermal output with increasing temperatures and durations of treatment. Polyethylene, treated with RFNA at 80 C for 40 hr, released 30 percent less thermal energy during combustion than unmodified polymer. These and other data obtained for chemically treated polyethylene are summarized in Table 8.

In subsequent studies, attempts were made to decrease the thermal output by exposing the polymer to mixed acids according to the nitration procedures used for synthetic fibers in the textile industry. Two solutions were prepared containing: (1) 56 parts HNO_3, 26 parts H_2SO_4, and 18 parts H_2O; and (2) 100 parts HNO_3 and 40.4 parts P_2O_5. Polyethylene samples placed in each of these solutions were treated at 80 C for 5, 10, and 20 hr. A significant decrease in the heat of combustion was observed in $HNO_3.P_2O_5$-treated polymer. The low heat of combustion (8,912 cal/g) obtained for polyethylene treated with the mixed system in comparison with HNO_3 alone (9,523 cal/g) indicated the greater effectiveness of the anhydride-containing acid. However, in all comparative tests, RFNA appeared to be the most damaging reagent for polyethylene.

The 10-percent reduction in the heat of combustion of chlorinated polyethylene indicated a relatively low degree of halogen substitution in the polyhydrocarbon following the chlorine treatment. To obtain quantitative information about the extent of halogen substitution in the laboratory-treated polyethylene, the heat of combustion of a commercial, unplasticized polyvinyl chloride* was also determined. The value of 4,580 cal per g obtained for this material was substantially lower than the 10,015 cal per g obtained for the chlorinated polyethylene. The hydrochloric acid (HCl) generated during combustion was equivalent to a chlorine content of 49 percent for commercial polyvinyl chloride as compared with 8 percent for the laboratory-treated polyolefin. It is therefore evident that a degree of halogenation greater than that realized in our experiments is necessary to maintain a low caloric output of the hydrocarbon.

Ozonization under relatively mild conditions appeared to have a small effect on the heat of combustion of polyethylene. Exposure to O_2 at elevated temperatures also did not perceptibly change the amount of heat dissipated by the sensitized polymer

*Pliovic WO-2, Goodyear Tire and Rubber Co.

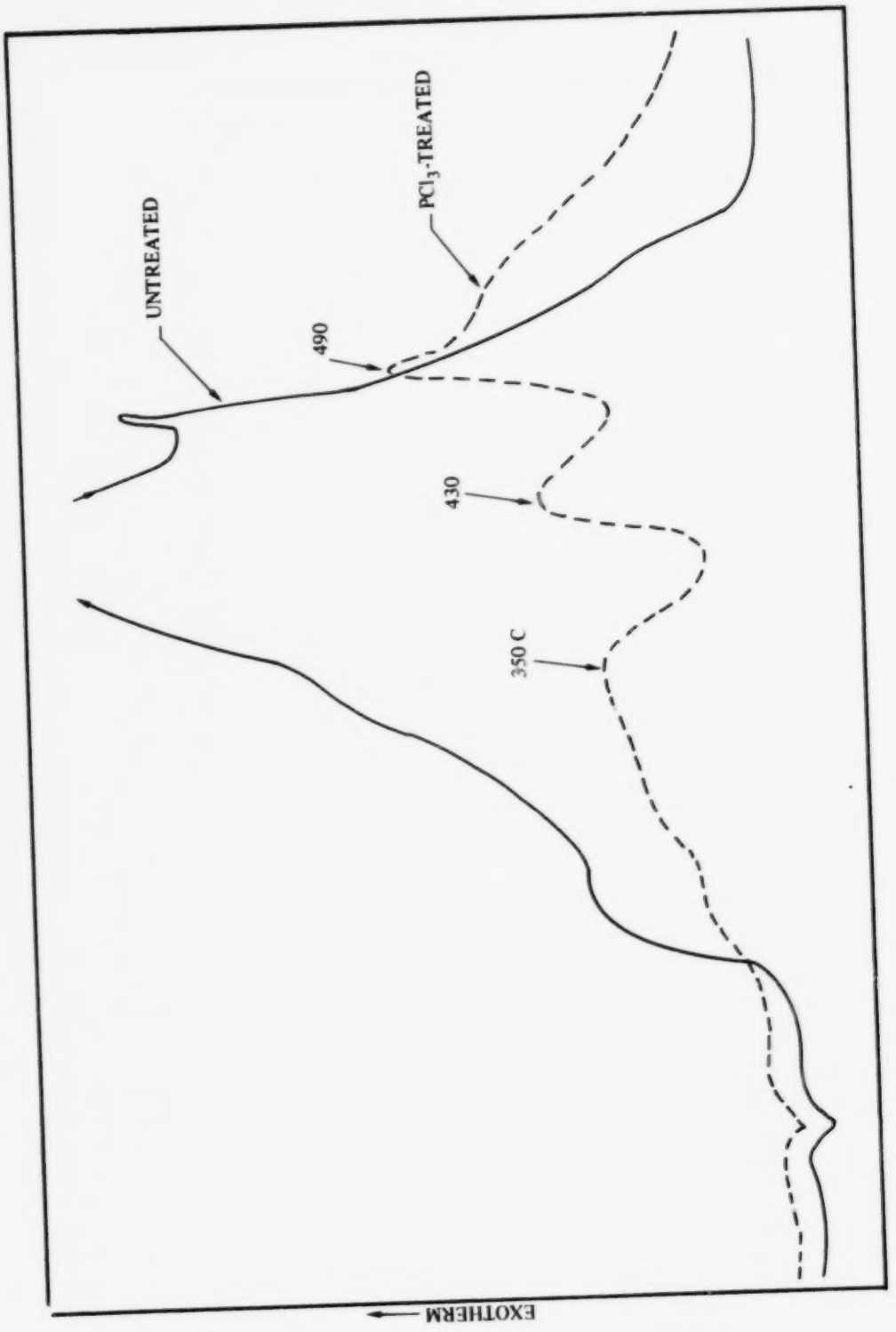


Figure 6. Differential thermograms of polyethylene before and after PCl_3 treatment.

TABLE 8

HEATS OF COMBUSTION OF TREATED POLYETHYLENE

Treatment			Duration (hr)	Temperature (C)	Heat of combustion (cal/g)
Oxidative	Degradation-promoting	Other			
None					11,064
RFNA			20	80	9,963
RFNA			40	80	7,991
HNO_3-P_2O_5			1	80	10,782
HNO_3-P_2O_5			5	80	9,847
HNO_3-P_2O_5			10	80	8,912
HNO_3-H_2SO_4			10	80	10,971
HNO_3-H_2SO_4			20	80	10,927
Ozone			46	40	10,922
Cl_2			20	80	10,015
NaClO			20	80	10,986
$NaClO_3$			20	80	11,045
	Benzoyl peroxide + O_2		20	80	10,688
	$FeCl_3$ + O_2		20	80	10,974
	$Co(NO_3)_2$ + O_2		20	80	10,901
	$Co(NO_3)_2$-$Mn(NO_3)_2$ + O_2		20	80	10,922
	$CoMoO_4$ + O_2		20	80	10,895
	$CoCrO_4$ + O_2		20	80	10,977
	Benzoin + UV		72	20	10,913
	2,4-dimethyl pentanone + UV		96	20	10,811
	2,2'-azobis(methyl)-propionitrile + UV		20	80	10,007
		Co^{60}, 100 megarads	--	--	10,948
		200 megarads	--	--	10,727
		400 megarads	--	--	10,605
		PCl_3	23	60	10,455
		PCl_3	20	25	9,744

during combustion. Ultraviolet radiation and exposure of polyethylene to gamma radiation at doses ranging from 100 to 400 megarads did not significantly affect the thermal output of Alathon 20, although the degradative influence of the radiation treatments was noticed in mechanical tests.

Infrared and Viscometric Studies. In an effort to determine the nature and extent of changes that occurred in the polymer as a result of chemical treatment, infrared measurements were performed parallel with the calorimetric studies on a series of selected specimens. Because the metal salts of the transition elements are known to affect polyolefins[70,71] and catalyze the oxidation of hydrocarbons,[72] an attempt was made to utilize these salts as possible catalysts for the

thermal oxidation and degradation of polyethylene and determine their influence on the chemical properties of modified polymer by infrared spectrophotometric measurements. Polyethylene samples in separate tests were treated for 4 hr at 100 C in three aqueous solutions containing by weight: (1) 11 percent $AgNo_3$, (2) 12.8 percent $CoMoO_4$, and (3) 11.2 percent $CoCrO_4$. After drying, the polymer was subjected to an oxidizing environment (O_2 admitted at a rate of 0.5 l/min) at 80 C.

Although the calorimetric measurements did not indicate significant changes in the heats of combustion of sensitized polyethylene, distinct differences were observed in the infrared spectrograms of these samples. The sensitization of polymer with $CoMoO_4$ and a mixture of $Co(NO_3)_2$ and $Mn(NO_3)_2$ (Figure 7) was more effective in promoting oxidative degradation than treatment with $Co(NO_3)_2$ or $CoCrO_4$ (Figure 8). The absorption bands in the 8.7- to 9.4-μ region, representing C-O stretching modes of aliphatic ethers, are more pronounced for $CoMoO_4$ - and $Co(NO_3)_2$-treated polyethylene than for the untreated material. However, the degradation-promoting activity of these catalysts was by no means sufficient to induce major thermal or mechanical changes in the oxidized polymer. Similar results were also obtained with benzoyl-peroxide-treated polyethylene (Figure 9). The appearance of the absorption band at 5.9μ, characteristic of a C-O stretching mode, is indicative of the chemical change in the polymer. The $FeCl_3$-catalyzed polyethylene subjected to UV radiation (Figure 10) and gamma-irradiated polyethylene (Figure 11) also exhibited carbonyl (C=O) bands, because partial destruction of bonds during irradiation caused the saturation of these bonds by available O_2 (air). In neither case did oxidation result in mechanical failure of the polymer.

More obvious effects of polymer degradation were found in polyethylene subjected to RFNA treatment. The pronounced brittleness of this material necessitated the preparation of 0.010-in.-thick films to prevent fracture of the compression-molded polymer during mounting of infrared specimens. This thickness reduced the transparency of the specimen and made resolution of the major absorption peaks difficult. Figure 12 represents the infrared spectrograms of untreated and RFNA-exposed polyethylene. Both specimens were prepared by compression molding. The peaks at 6 and 6.2 μ, representing NO_2-stretching modes, are missing in the control specimen. Symmetric NO_2-stretching modes at 6.7 to 8.0 μ are obscured by intense absorption bands in this region. The two absorption peaks at 10.9 and 12.0 μ represent C-N vibrations of attached NO_2 groups. Their absence in the untreated polymer indicates the effectiveness of the nitration treatment. Although the spectroscopic method was qualitatively helpful in identifying the NO_3 functionality of RFNA-treated Alathon 20, the technique could not be used for quantitative measurements because of the fragility of thin, nitrated films. Therefore, analytical methods for nitrogen analysis had to be used to determine the extent of polyethylene nitration in relation to the duration of treatment.

The oxidative chain scission resulting from exposure of polyethylene to RFNA was assessed from viscometric measurements performed on treated polyethylene in xylene solution. Problems arising from the precipitation of polymer from solution at higher concentrations made the analysis of data unreliable in terms of intrinsic viscosities. Therefore, the viscosity-exposure duration relationship of RFNA-treated polyethylene was determined at a relatively low concentration, 1×10^{-3} g per ml, for which the solute remained completely in solution. Under these conditions, the relative viscosities (normalized with respect to the solution

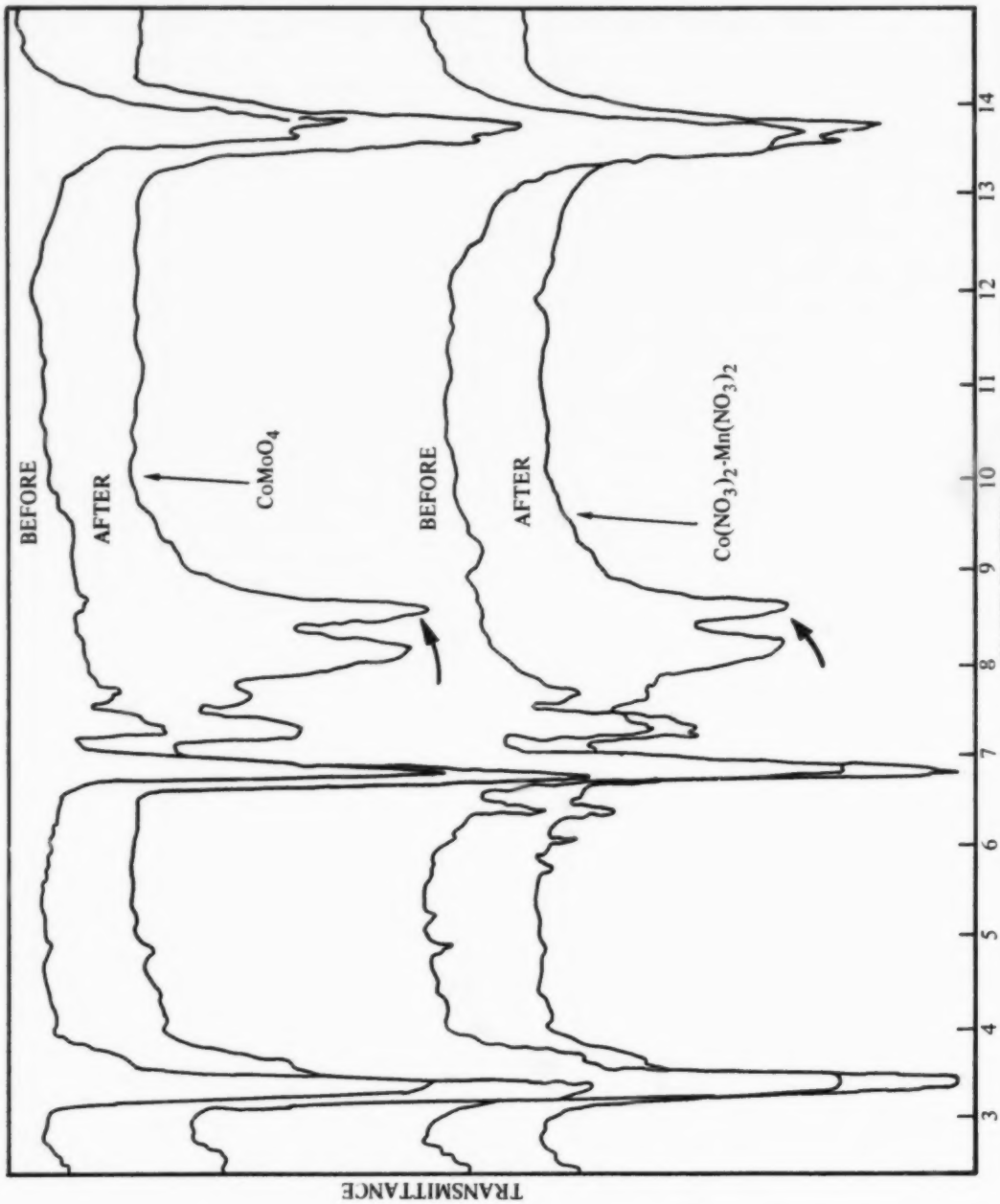


Figure 7. Infrared spectrograms of polyethylene sensitized with $CoMoO_4$ and $Co(NO_3)_2$-$Mn(NO_3)_2$ before and after oxidation.

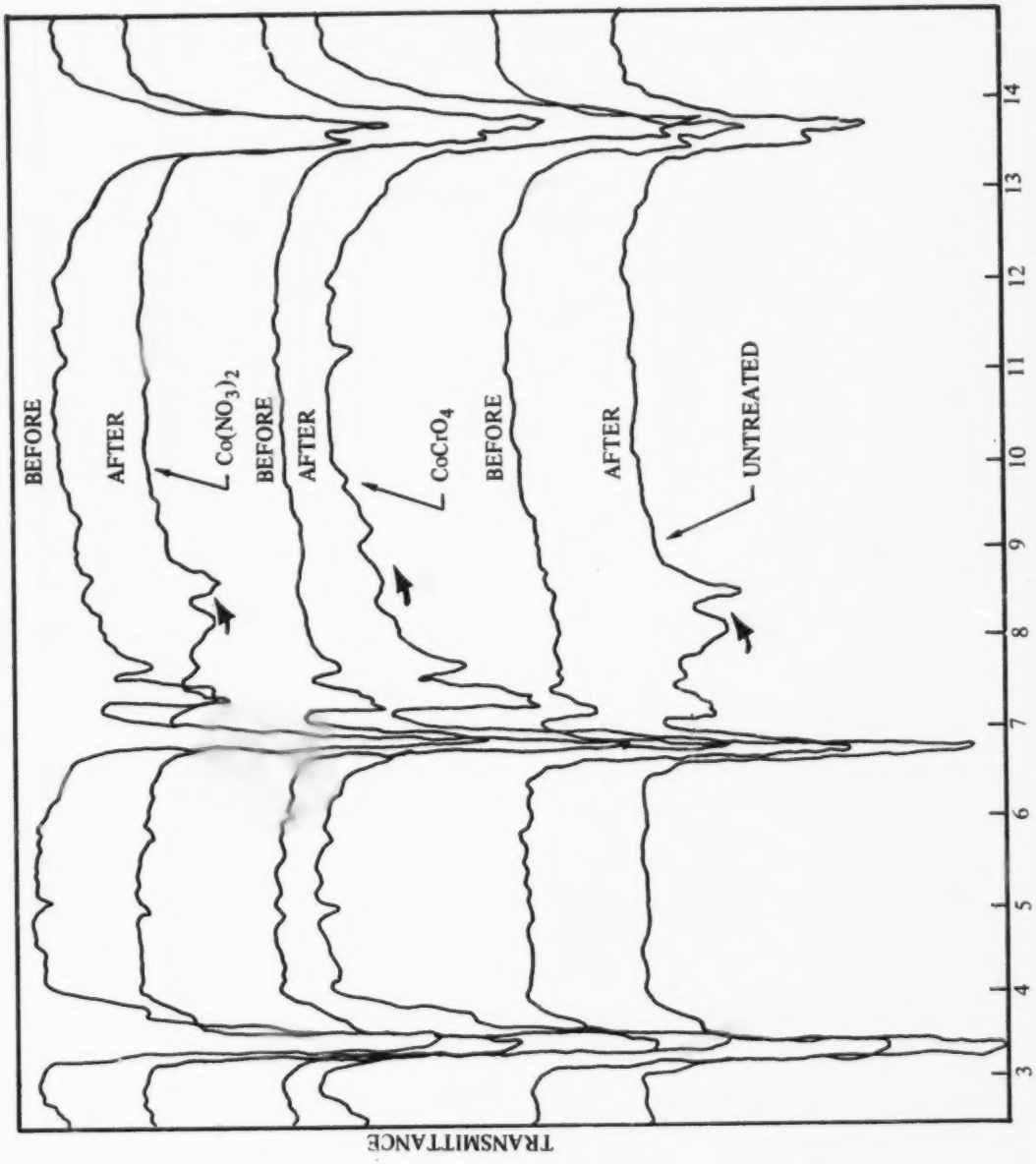


Figure 8. Infrared spectrograms of polyethylene sensitized with $Co(NO_3)_2$ and $CoCrO_4$ before and after oxidation.

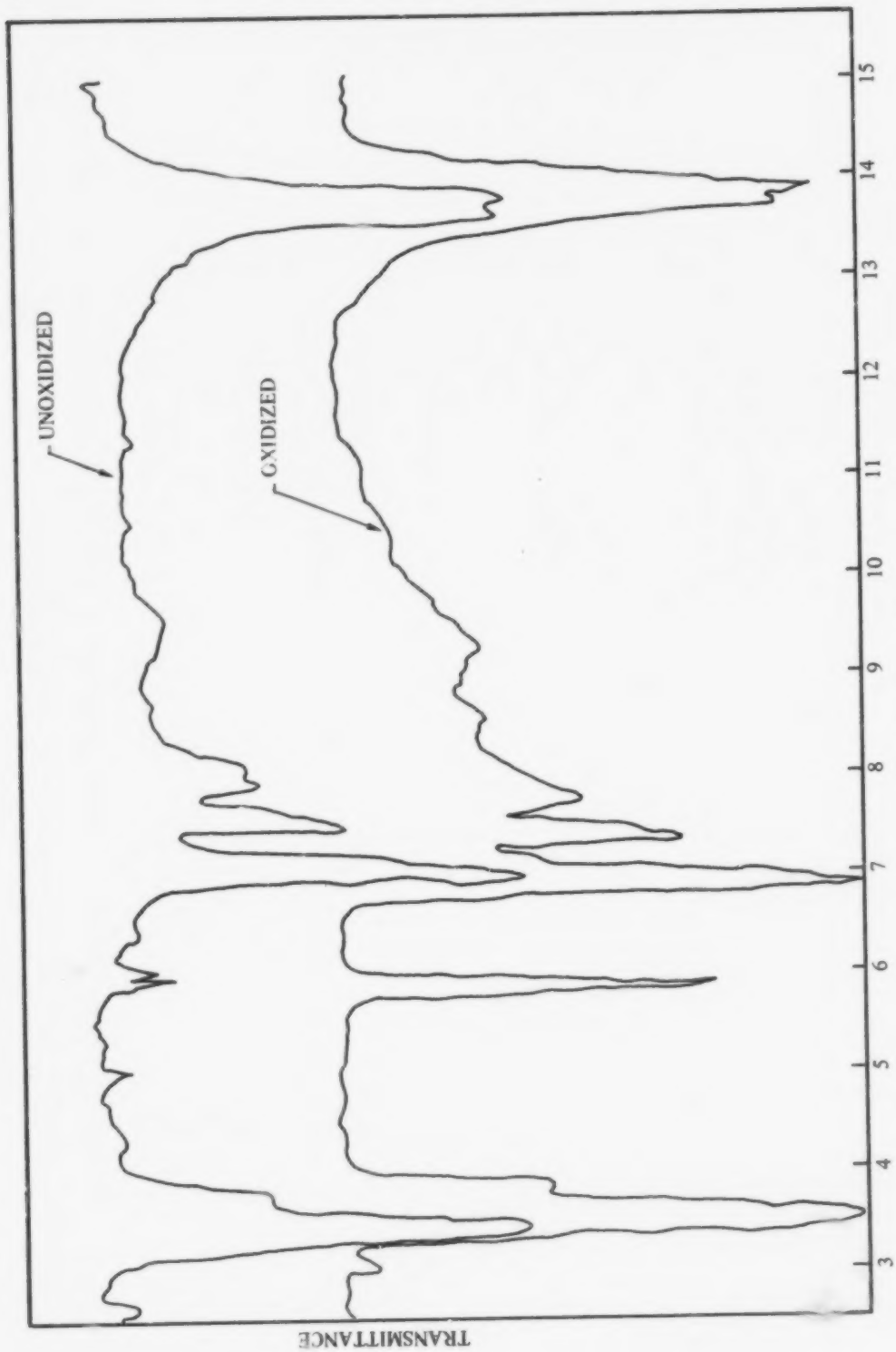


Figure 9. Infrared spectrograms of benzoyl-peroxide-treated polyethylene before and after oxidation.

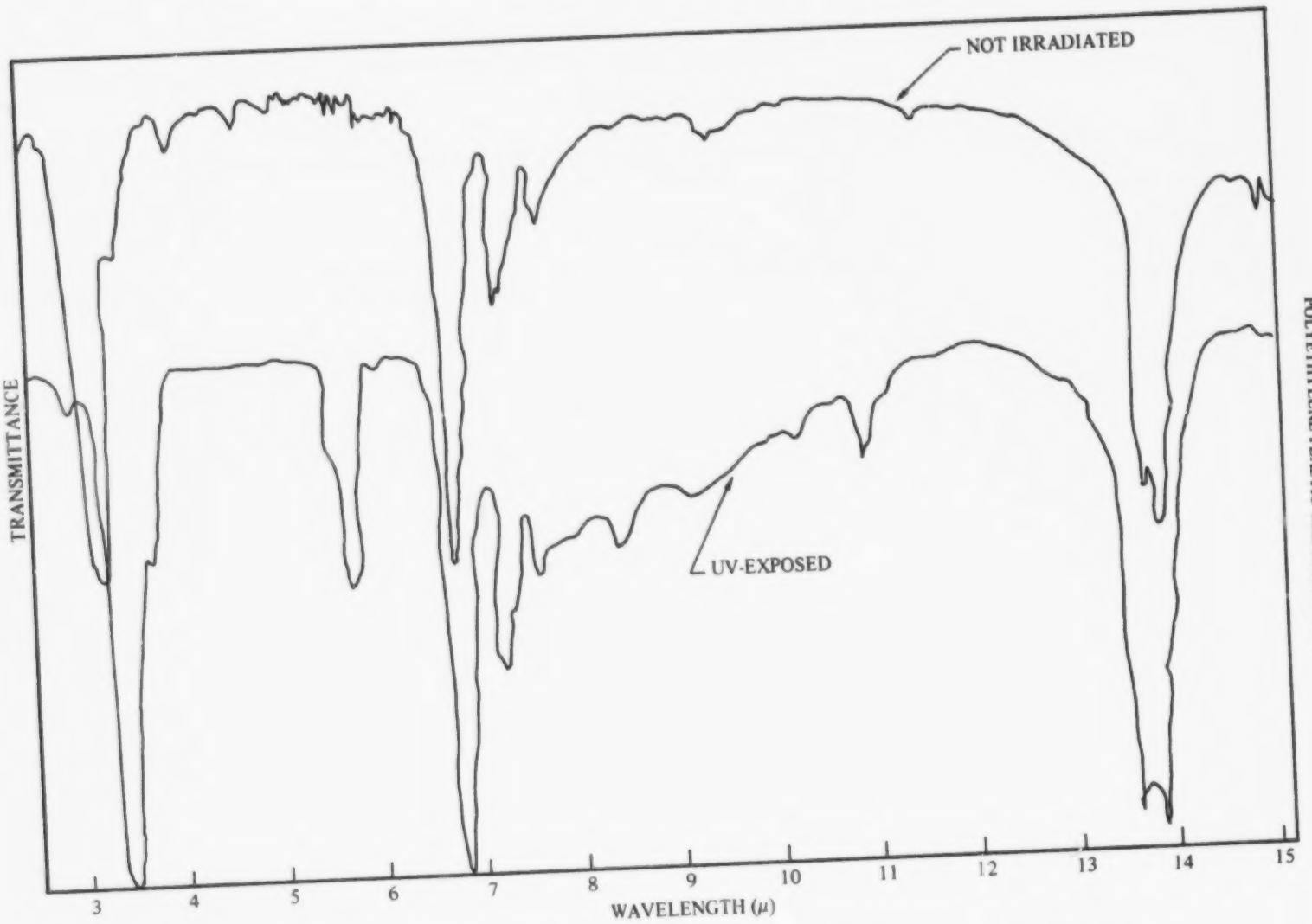


Figure 10. Infrared spectrograms of $FeCl_3$-treated polyethylene before and after exposure to UV radiation.

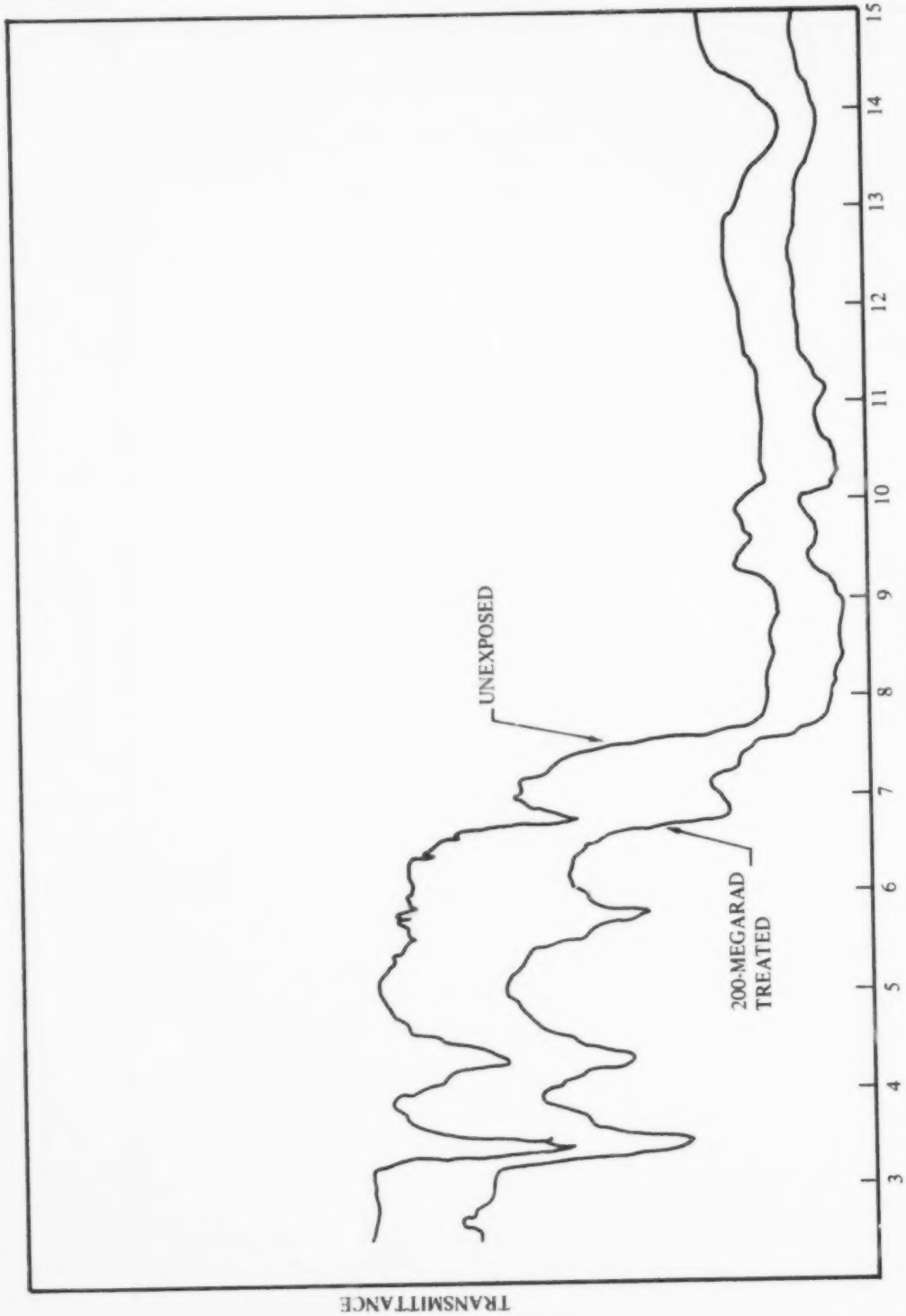


Figure 11. Infrared spectrograms of unexposed and gamma-irradiated polyethylene.

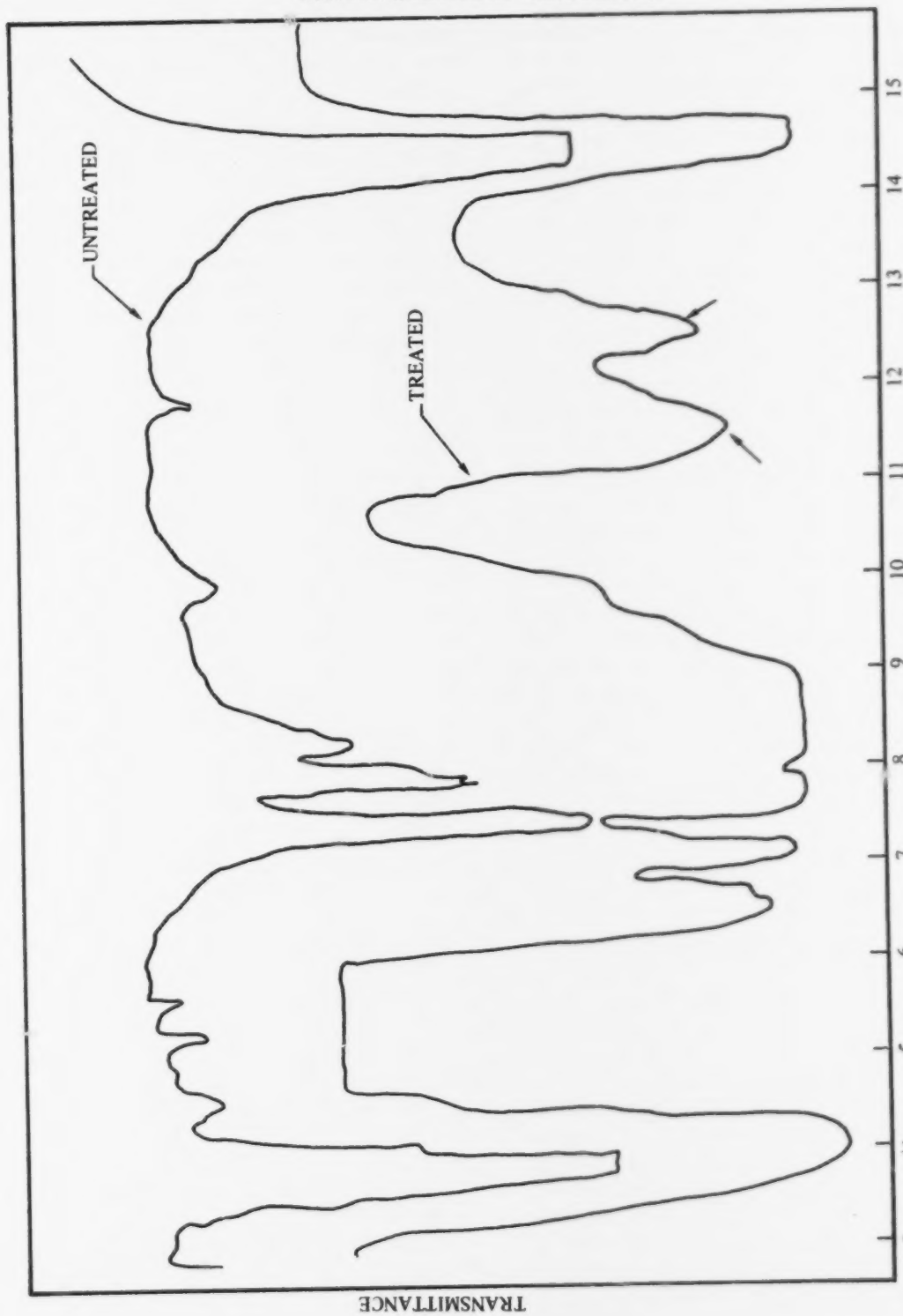


Figure 12. Infrared spectrograms of untreated and RFNA-exposed polyethylene.

density) remained in the proportion 3.5:1.3:1.1:1.0 for untreated polyethylene and polymer that was treated with RFNA for 10, 20, and 40 hr, respectively. The threefold reduction in viscosity of polyethylene subjected to RFNA treatment for 40 hr indicates the appreciable decrease in molecular weight of the treated material. Bond scission induced by extended exposure of polyethylene to RFNA is not as pronounced as changes in other properties, such as mechanical behavior and degree of nitration, would suggest. As far as viscosity relationships are concerned, the main damage appears to be incurred by the polymer in the first 10 hr of RFNA exposure.

Mechanical Properties. The changes in the structural integrity of polyethylene after exposure to degradation-promoting conditions were investigated by mechanical test methods involving rapid compression of cylindrical test specimens. The rod-like specimens were extruded on a Killian 1:24-in. extruder at 400 F. In one series of experiments, the mechanical properties were determined for rods exposed in bulk to the degradation-promoting conditions, while in other experiments polyethylene pellets were subjected to chemical treatment and the treated specimens were subsequently prepared. Measurements were performed on a high-speed testing machine at a compression rate of 4,000 in. per min.

The oscilloscope tracings for samples compressed to 50 percent of their initial height are shown in Figure 13. As indicated, the maximum compressive strengths of the polymer after short-duration RFNA and N_2O_4 treatment are respectively 93.4 and 7.17 percent of the initial value. Similar relationships are also observed for the plateau stress values of compressed specimens. Under the relatively mild exposure conditions used in preliminary tests, N_2O_4 appeared more effective in reducing the strength of polyethylene than RFNA. The temperature used in the treatment and the degree of subdivision of the polymer during treatment affected the mechanical properties as shown in Table 9.

It should be emphasized that appreciable changes in appearance were noticed in the rods extruded from the polyethylene pellets after the pellets received the selected treatments. A pronounced brown discoloration was found in cylinders that were extruded from pellets treated for 5 hr at 20 C with N_2O_4. Similar effects were observed for polyethylene subjected to RFNA at 80 C for 10 hr. After treatment with this oxidizing acid for 20 hr, the washed and dried polyethylene pellets were completely fluidized when subjected to elevated temperatures in the extruder. Under these conditions the polymer could no longer be extruded into rods. Therefore, it became necessary to mold cylindrical specimens from the fluidized plastic at a lower temperature (150 C). The solidified specimens that were obtained, unlike polyethylene, exhibited the properties of melt viscosity and the brittleness of a low-molecular-weight paraffin. Brittleness was indicated by the tendency of specimens to shatter into small pieces when dropped from a height of 8 ft and to pulverize when hit with a hammer.

The effects of chemical treatment on the mechanical properties of polyethylene were also investigated at low rates of loading (0.5 in./min) in a test designed to determine the crushability of modified polymer. Tests performed on disklike specimens did not permit determination of the ultimate crushing force, because an abrupt change in the impressed force could not be discerned under the experimental test conditions. Therefore, the specimens were compression loaded to 30 lb at a rate of 0.5 in./min, and the decay in impressed force was followed for 5 min. Additional information about the compressive strength of the material was also obtained from the initial slope of the load-deformation curve in the early strain cycle. The results, summarized in Table 10, indicate 10, 35, 68,

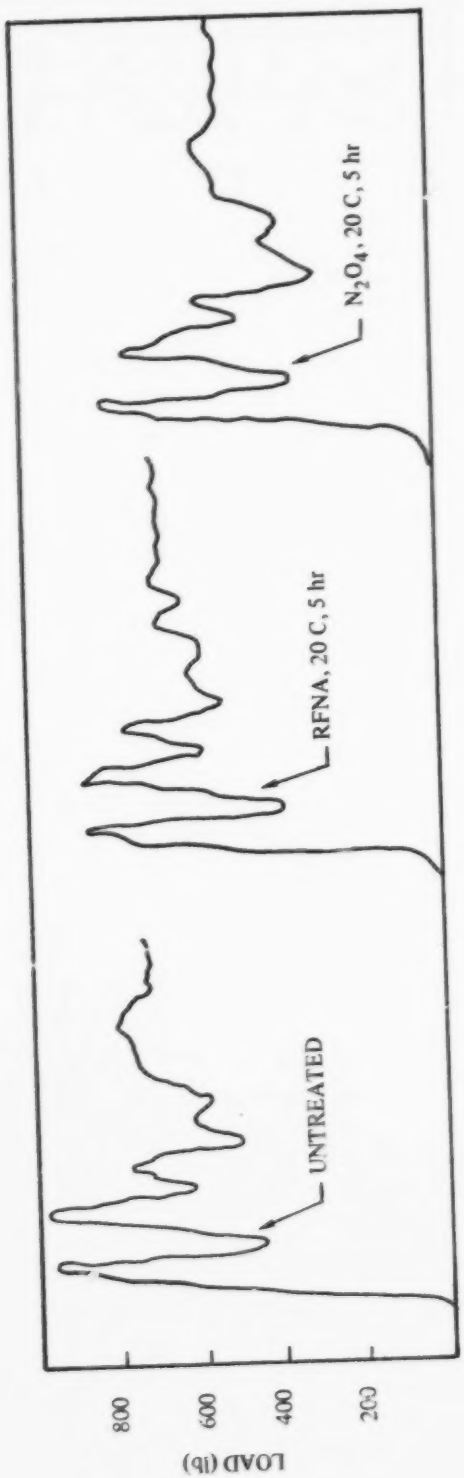


Figure 13. Oscilloscope tracings of compression-loaded polyethylene.

TABLE 9

MECHANICAL BEHAVIOR OF TREATED POLYETHYLENE IN HIGH-SPEED COMPRESSIVE TESTS

Treatment conditions	Compressive stress (psi)					
	Untreated		RFNA		N_2O_4	
	Initial	Plateau	Initial	Plateau	Initial	Plateau
Rod, untreated	7,030	5,316				
Rod, 20 C, 5 hr			6,145 (87)*	5,166 (97)		
Rod, - 10 C, 5 hr					6,549 (93)	5,266 (99)
Pellet, 20 C, 5 hr			5,985 (85)	4,968 (93)	5,160 (73)	3,815 (72)
Pellet, 20 C, 20 hr					6,133 (88)	4,928 (93)
Pellet, - 10 C, 5 hr					5,679 (81)	5,108 (96)

*The figures in parentheses indicate the relative compressive strengths of treated polyethylene, in percent, in comparison with the parent material.

TABLE 10

MECHANICAL BEHAVIOR OF POLYETHYLENE IN COMPRESSION

Treatment	Initial load-deformation slope (lb/in.)	Relaxation		
		Initial load (lb)	Load after 5 min (lb)	Change (%)
None	64.2	30.3	17.4	9.8
Co^{60}, 400 megarads	83.0	29.8	15.1	49.2
PCl_3, 25 C, 20 hr	66.6	29.9	19.4	35.4
HNO_3-H_2SO_4, 80 C, 10 hr	58.8	29.5	9.3	68.2
HNO_3-P_2O_5, 80 C, 10 hr	15.0	29.7	5.8	80.7

and 81 percent reductions in the load-carrying capability of untreated polymer and polyethylene exposed to PCl_3, HNO_3-H_2SO_4, and HNO_3-P_2O_5, respectively.

The exposure of polyethylene to chlorine resulted in a very dark discoloration of the modified polymer during extrusion. This enhanced decomposition could be attributed to the presence of bound chlorine on the polyolefin and the thermolytic cleavage of hydrogen halide during extrusion, which accelerated the degradation of polyethylene. The temperature for incipient thermal degradation would then be shifted toward lower values, thus accounting for the instability of the chlorine-treated polymer at normal extrusion temperatures.

Ozonization appeared to have the opposite effect from chlorination on the extrusion behavior of oxidized polymer. As a result of partial cross-linking, the ozonized plastic resisted extrusion. The lower heat of combustion of O_3-treated polyethylene in comparison with the parent material suggests that bond scission occurred concurrently with cross-linking. The inherently flexible plastic becomes relatively brittle if the cross-linking effects outweigh the bond-scission process during prolonged exposure of polyethylene to O_3. In our experiments, the O_3 doses did not produce these effects, and the polyethylene retained a fair degree of flexibility.

In an effort to enhance the brittleness of polyethylene, two parallel experiments were performed on rod and sheet specimens exposed to a stress-crack-sensitizing medium. A 0.004-in.-thick polyethylene sheet subjected to biaxial tension equivalent to 25 percent elongation was treated with a surface-energy-reducing, crack-promoting fluid*. After 2 weeks, the film, mounted in a multiclamp biaxial stretch device, developed small cracks in the direction of film extrusion. A similar effect was also observed in rods of 0.5-in. diameter when these rods, subjected to multiaxial stress by 0.3-in.-tapered aluminum insertions forced into them, were immersed in the surface-energy-reducing fluid. Craze marks, clearly visible under the microscope, developed at the periphery of the stressed specimens. However, the imperfections did not affect the mechanical properties of the rods or sheets significantly enough to suggest the applicability of the stress-crack approach as a method for enhancing the disposal of bulk polyethylene by promoting its embrittlement. In this regard, the RFNA treatment was much more effective for promoting embrittlement, because it converted the inherently flexible plastic into a rigid and rather fragile material. Other potential advantages derived from the nitrating procedure and relating to the conversion of polyethylene into a biodegradable material were investigated in subsequent studies.

Biochemical and Analytical Investigations. The changes in the mechanical and thermal properties of polyethylene exposed to RFNA suggested the desirability of investigating the changes in the chemical behavior of the treated polymer, particularly with regard to the extent of polyolefin nitration, as residual nitrogen could enhance the biodegradability of the polymer by the nitrogen-utilizing microorganisms. Consequently, the residual amount of nitrogen in polyethylene subjected to different nitration treatments was determined by the previously discussed micro-Keldahl method. The results are summarized in Table 11.

The percentage of residual nitrogen after treatment at room temperature was relatively low. Prolonged exposure at elevated temperatures increased the amount of nitrogen to 3.8 percent after a 40-hr treatment. Even better results were obtained from two-component systems, particularly with HNO_3 and P_2O_5, in which the final amount of nitrogen after 5 hr at 80 C was 3.1 percent.

*Igepal CA-630, General Aniline and Film Co.

TABLE 11

NITROGEN CONTENT IN TREATED POLYETHYLENE

Compound	Treatment		Nitrogen content (%)
	Duration (hr)	Temperature (C)	
RFNA	5	20	0.21
RFNA	5	80	1.02
RFNA	10	80	1.52
RFNA	20	80	1.58
RFNA	40	80	3.82
$HNO_3 + H_2SO_4$	5	80	4.40
$HNO_3 + H_2SO_4$	10	80	4.60
$HNO_3 + H_2SO_4$	20	80	4.82
$HNO_3 + P_2O_5$	1	80	1.42
$HNO_3 + P_2O_5$	5	80	3.14

In an effort to determine the susceptibility of chemically treated polyethylene to biodegradation, six specimens that had received different treatments were exposed to selected organisms in an inoculated agar system under the conditions described in the previous section on methods. The samples investigated included untreated plastic, as well as ozonized, chlorinated, N_2O_4- and RFNA-treated polyethylene. The attack by fungal organisms of these samples was determined in a nitrogen- and dextrose-depleted, minimal-salt agar medium to obtain information about the selective utilization of carbon and nitrogen from the plastic source by the organisms. The positive control for these experiments provided the minimal-salt agar medium to which 1 percent dextrose was added. None of the tested polymer specimens revealed fungal growth after a 28-day exposure to the microorganisms, but the carbohydrate-containing control was heavily invaded by fungi.

The negative results obtained from exposing treated polyethylene to fungi suggested the need to extend the biological investigations to bacterial microorganisms. The use of bacteria appeared desirable because of their more rapid growth rate in comparison with fungi. Two strains of *Pseudomonas aeruginosa* were used in investigations conducted with polymeric specimens dispersed in minimal-salt broth media buffered at pH 7. The composition of the medium is shown in Table 12.

Tests were performed in media that had glucose and NH_4NO_3 selectively omitted from the broth system to determine the extent of polymer utilization as a source of carbon or nitrogen for the organisms considered, and a complete medium was used for control studies. Visual determination of bacterial growth disclosed little change in inoculated polymer systems during the first 2 days of observation. However, after 72 hr, the polyethylene that received the RFNA treatment at 80 C for 40 hr exhibited noticeable bacterial growth. Ozonized and chlorinated polyethylene, as well as polymer exposed to RFNA for less than 40 hr, showed no visible changes over a 10-day period, after which the test was terminated. It should be emphasized that the 40-hr-exposure condition

does not represent the optimum treatment for obtaining a maximum amount of residual nitrogen. However, at the time when the biochemical tests were conducted, the information on the efficiency of acid treatment in mixed systems was not available. Therefore, it is quite possible that the extent of bacterial attack on modified polyethylene could be further increased by prior exposure of polymer to HNO_3-H_2SO_4 or HNO_3-P_2O_5. The selective removal of nitrogen from nitrated polyethylene should greatly weaken the polymer structure and effect its degradation. Thus the use of more effective treatments deserves consideration in future studies of the degradation of polyethylene by biological methods.

TABLE 12

COMPOSITION OF BROTH MEDIUM FOR BACTERIAL GROWTH STUDIES

Constituent	Concentration (g/l)
KH_2PO_4	1.34
$Na_2HPO_4 . H_2O$	4.08
$MgSO_4$	0.02
Glucose	10.00
NH_4NO_3	2.00

CONCLUSION

The chemical and biological inertness of polyethylene, which is primarily due to its hydrocarbon nature and its ordered structure, makes the disposal of polyolefin waste by chemical and biological methods difficult. However, despite this difficulty the experimental studies conducted in the course of this program have shown that chemical treatment of plastic can modify the mechanical, thermal, and biochemical properties of the material in such a way as to facilitate the ultimate disposal of plastic. The approach that has appeared particularly attractive involves the oxidative degradation and concomitant nitration of polyethylene by exposure to RFNA, or binary systems including HNO_3, as a constituent. Considerations for this approach follow.

- Thermal treatment of polyethylene, following exposure to HNO_3, resulted in pronounced embrittlement of this inherently flexible plastic to the extent that it could be shattered by impact force. This behavior is important in the disposal of polyethylene, because effective compaction reduces the volume of solid waste and minimizes space requirements in landfill and incineration processes.
- Thermal response of acid-treated polyethylene changed noticeably in comparison with untreated material, as indicated by DTA and calorimetric measurements. A 30-percent reduction in the heat of combustion was observed for the oxidized polymer. This reduction represents the additional benefit that could be derived from the oxidizing-acid treatment, because a lowered heat output should extend the life of gratings and other furnace components. The exposure of polyethylene to chlorine had a similar, although much less pronounced (10% reduction in the heat of combustion) effect.
- Although polyethylene resists attack by fungal and bacterial microorganisms, nitration modified the polyhydrocarbon to an extent that its utilization by bacteria (Pseudomonas) became apparent after a 72-hr exposure. The residual amount (3.8%) of nitrogen in modified polyethylene used in these

experiments does not represent the maximum nitrogen content. The attack of polymer by selected microorganisms could probably be enhanced by treating the hydrocarbon with binary acids to produce higher nitrogen yields. In this regard, the possible utilization of nitrogen-(or phosphorus-) containing polyolefins as soil conditioners or fertilizers deserves attention.

- Efforts to enhance the degradation of polyethylene by ozonization or by exposure to ultraviolet light and gammairradiation did not produce large enough effects to warrant the use of these methods for facilitating the disposal of polyolefin waste. Some of the difficulties encountered in promoting the disintegration of polymers might relate to the ineffective methods of applying sensitizing agents and catalysts to the plastic. These compounds were essentially applied to the surfaces of the high-molecular-weight materials on which they exhibited only limited effectiveness. Adding the agents to the polymer after initiation of the degradation process by thermal oxidation or irradiation should influence the mechanical and physical properties of polyethylene, because degradation would occur throughout the bulk of the material.

The foregoing considerations indicate the desirability of continuing the studies on the disposal of polyethylene waste by chemical treatment. Attention should be given to the degradation of the polymer in multicomponent oxidizing systems, the effects of the latter on biodegradability, and the use of selected catalysts. Following sanitary landfilling, special studies should be made to determine if there could be groundwater pollution due to leaching of the treated polyethylene. The aspects of air pollution by combustion products of parent and chemically modified polyethylene deserve attention, and particular consideration should be given to the use of combustion-promoting and pollutant-reducing compounds. These studies should be extended to other commercially important vinyl polymers, such as polyvinyl chloride and polystyrene, to determine the applicability of the selected methods in a more comprehensive study of polymer waste treatment.

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